

CHAPTER 5

MESOGENIC CRYSTAL STRUCTURES AND MOLECULAR PACKING

5.1 Early X-ray work on mesogenic compounds

Though compounds exhibiting liquid crystalline behaviour have been known for over 85 years, X-ray analysis of the crystalline as well as the liquid crystalline forms has received very little attention until recently. In particular, single crystal X-ray work has gained interest only during the last ten years. The earliest X-ray studies on liquid crystals dates back to 1921 when Huckel [1] attempted to understand the packing of molecules in mesophases. He observed that the diffraction patterns from nematic mesophases resemble those of isotropic liquids, indicating an absence of three-dimensional order. Friedel [2], in 1925, showed that the smectic phase consists of equidistant parallel layers. In 1927, Kast [3] studied magnetically aligned nematic phase of *p*-azoxyanisole using X-rays and observed two diffuse diffraction maxima. Hermann and Krummacker [4] have reported X-ray powder analyses of some mesogens.

Bernal and Crowfoot [5], in 1933, were the first to undertake the crystal structure analysis of mesogens using single crystals. They studied by X-ray and optical

methods **several mesogenic** compounds, viz., **p-azoxyanisole**, **p-aeoxyphenetole** and **anisal 1:5 diamino naphthalene**, all of which exhibit **nematic mesophases**; two **isomorphous cholesterogenic** compounds, viz., **cholesteryl chloride** and **cholesteryl bromide**; and **dibenzylidene benzidine**, **ethyl anisal p-aminocinnamate**, **ethyl phenyl benzylamino cinnamate** and **diethyl p-xylidine-bis aminocinnamate** which form **smectic liquid crystals**. They determined the **principal** optic directions for all these compounds, and the unit cell **dimensions** and space groups of **all** except the last two compounds in the list. **Combining** the preliminary data with the **intensities** of a few **very** intense X-ray **reflections**, they have fixed within fairly narrow limits the **positions** and orientations of the **molecules** within the unit **cell**, which in turn gave the scheme of the molecular **packing** in the crystal. They **observed** a **parallel** arrangement of **nematogenic** molecules in their respective crystalline phasee. This was found to be very similar to the type of molecular arrangement expected in their nematic **mesophases**. They refer to this type of **molecular arrangement** as 'imbricated', implying thereby that the end of one molecule is overlapping on a **neighbouring** molecule. They also observed that **in** the crystalline phase, smectogenic molecules **pack** in layers, The moleoular arrangement in each liquid **crystalline** phase is specific and is most often related to the

molecular arrangement in the respective crystalline phase also. Later studies on crystal structures of mesogens have confirmed that nematogens generally have an imbricated molecular packing, as contrasted with the layered packing arrangement found in smectogens.

Bernal and Crowfoot report that besides the 'sharp reflections', the X-ray photographs of most of these mesogenic compounds contained blurred Lines, known as 'smear lines'. Similar 'smear lines' were earlier observed in the photographs of certain minerals like asbestos and mica, which have sheet-like structures. They attribute these 'smear Lines' to diffuse reflections from certain planes of the reciprocal lattice, whose plane normals are parallel to the molecular length and mention that the molecules are likely to have a certain freedom of translatory movement along their long molecular axes. The translatory freedom of motion could eventually lead to disorder in the structure which in turn gives rise to the 'smear lines'. They have used this feature also in predicting the molecular orientation in the liquid crystalline phase.

The crystal structures predicted by Bernal and Crowfoot very well accounted for the optical properties of the compounds but agreed only qualitatively with the with the X-ray diffraction patterns. Nevertheless, their

classic work based on meagre X-ray data is extremely valuable.

5.2 Mesogenic crystal structures

From 1933 to 1968, **structure determination** of mesogenic **compounds** using single **crystals** did not receive much attention. However, in recent years, crystal structure analysis of **mesogens** has gained **considerable** interest and a large number of **crystal** structures have been reported. A great deal of X-ray work on the various **mesophases** themselves has **also** been reported. The account given in this section concerns only with the results of the X-ray investigations in the orystalline phase and, in **particular**, with single **crystal** analysis. A summary of the common **and** prominent structural characteristics which have emerged out of these analyses is given below, with special emphasis on the mode of **packing** in the **crystal**. For the sake of completeness, the early work of Bernal and **Crowfoot** **has** also been included in this listing.

(a) Nematogenic Crystal Structures

- (i) **p-azoxyanisole**, PAA (stable form) [5,6,7,8,9],
Figures 5.1 and 5.2.

Bernal and **Crowfoot** [5] report the presence of 'smear lines' on the X-ray photographs of PAA. **Carlisle** and **Smith** [6] suggest that the presence of 'smear lines'

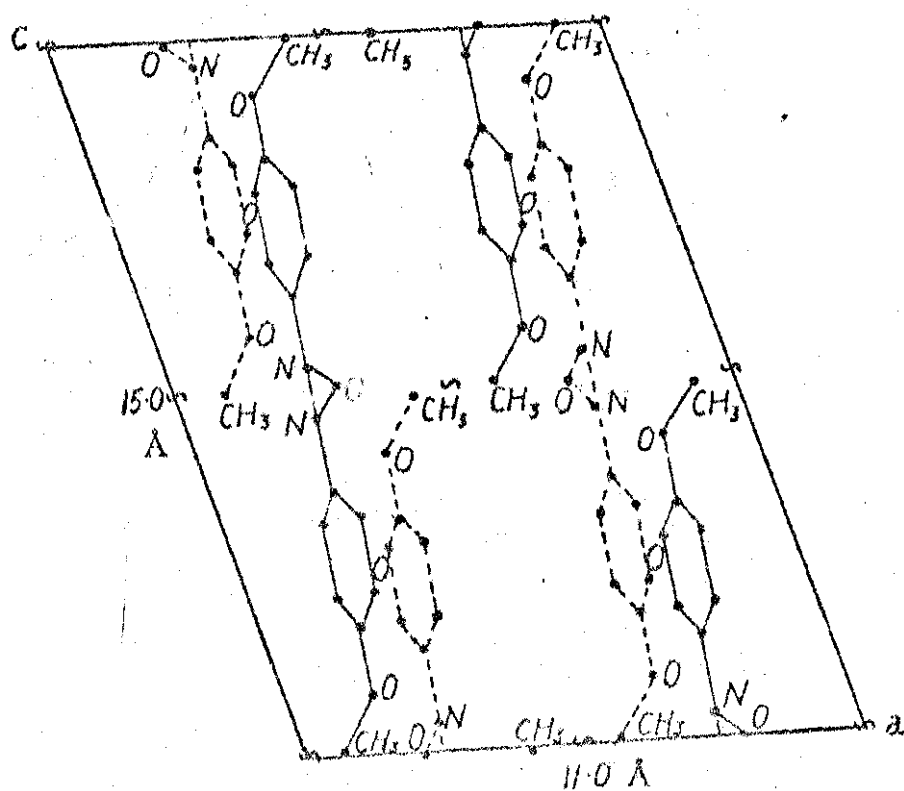


Figure 5.1: The molecular arrangement for PAA predicted by Bernal and Crowfoot [5].

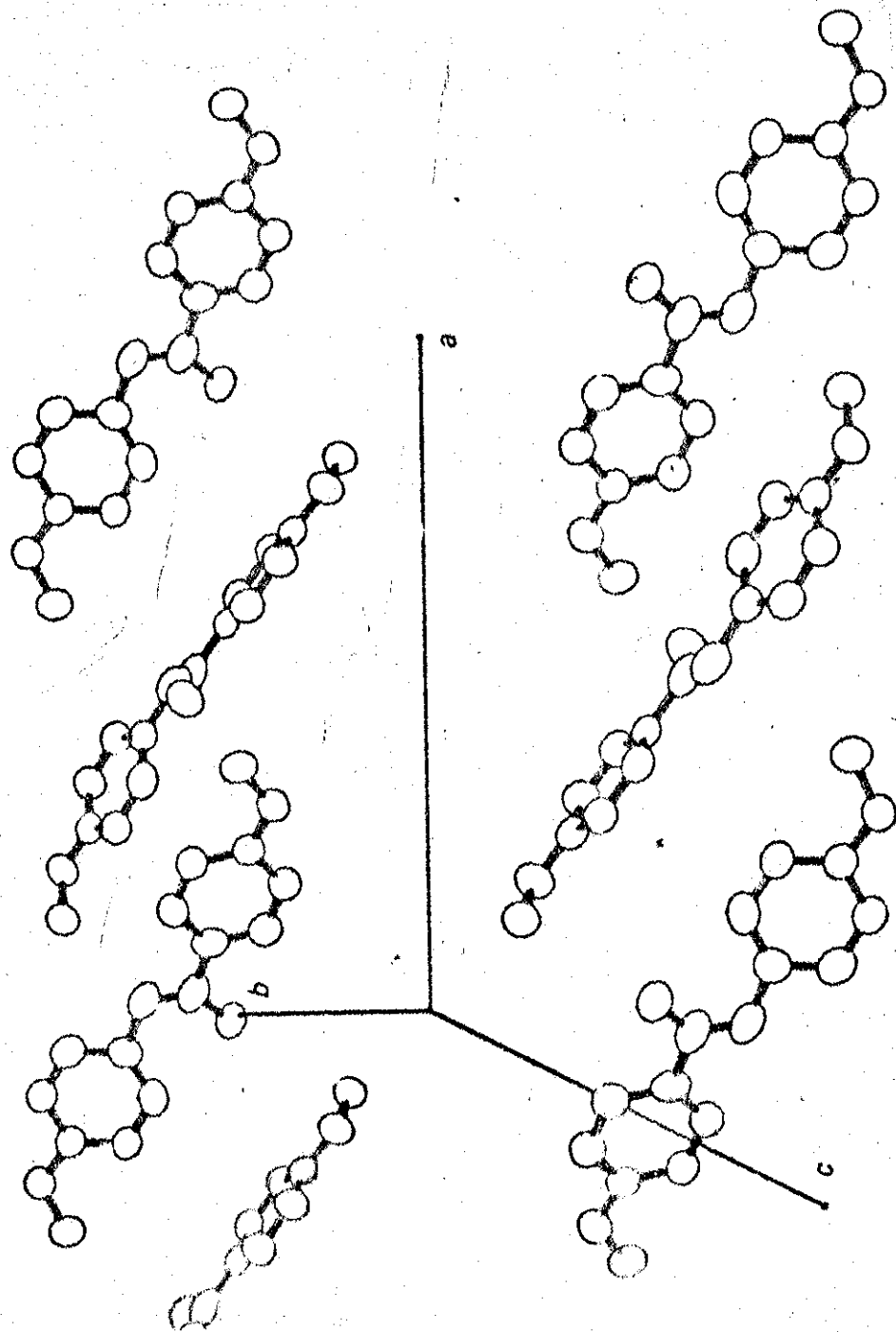
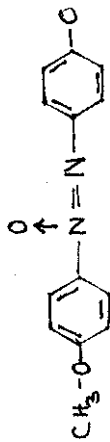


Figure 5.2: The molecular packing in the crystal structure of PAA as obtained by Krigbaum et al. [7].

is due to the existence of **statistical** disorder involving the displacement of moleculea **parallel** to their long axea. **Bernal** and Crowfoot, however, do not mention any disorder, The later accurate work of **Krigbaum et al** [7] **does** not support the presence of any such disorder. The **imbricated packing** of moleculea obtained by **Krigbaum et al** is in general conformity with the **predictions** of Bernal and Crowfoot. The **methoxy** group of one molecule is nearly in contact with the aeoxy group of its **neighbour**. The proximity of these active groups leads to the intermolecular **cohesive** forces.

(ii) p-azoxyphenetole [5] Fig. 5.3.

'**Smear** lines' were observed on the X-ray photographs. The **molecules** are imbricated and the **active** groups of **neighbouring molecules**, viz., the ether group of one molecule and the **azoxy** group of **the** other, **are** in close proximity.

(iii) Anisal 1:5 diamino naphthalene [5] Fig. 5.4a and Fig. 5.4b.

The **compound** has a **stable** solid form obtained from solution and **two** metastable forms obtained from the nematic **melt**. The authors feel that the oonsiderably **interlocked** molecular arrangement shown in Fig. 5.4(a) and Fig. 5.4(b) may not **correspond** to the arrangement in

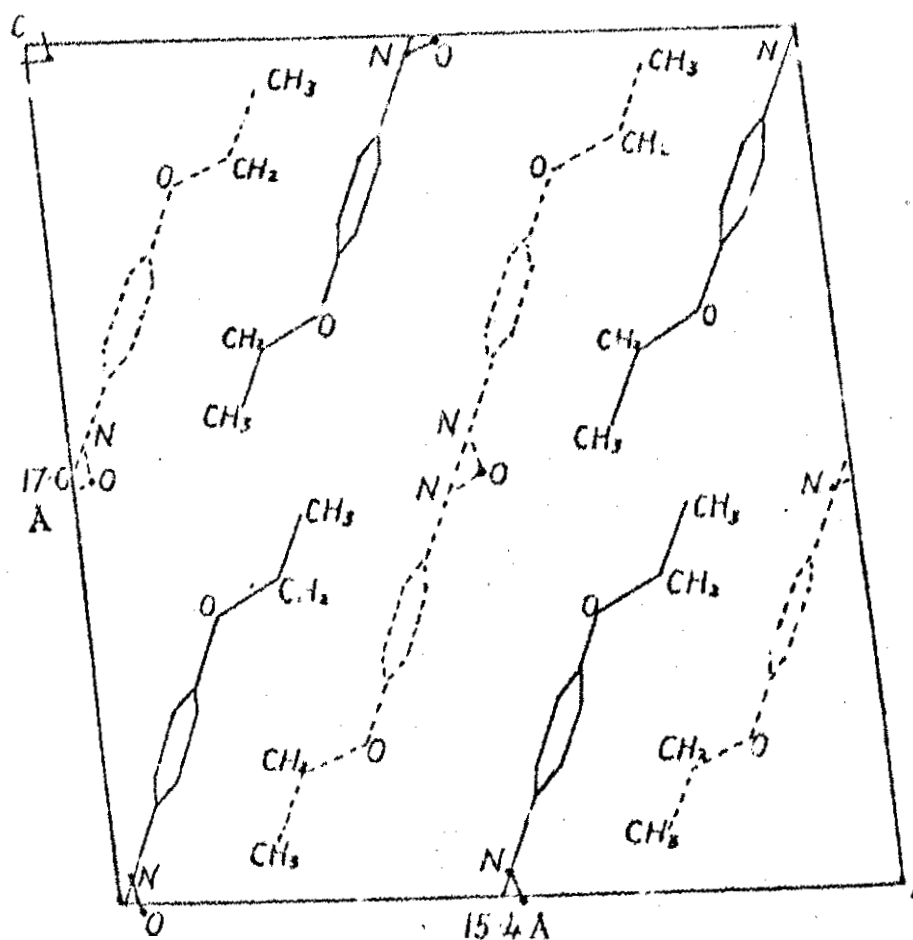
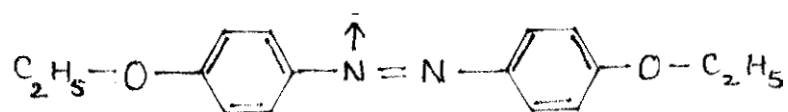
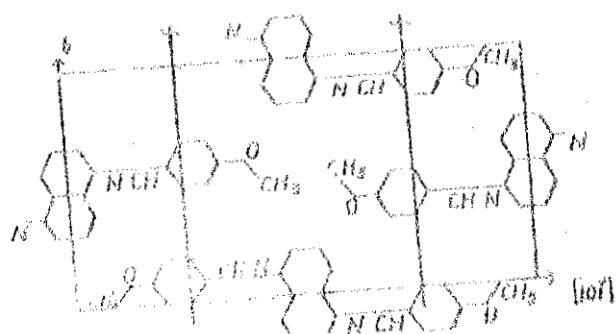
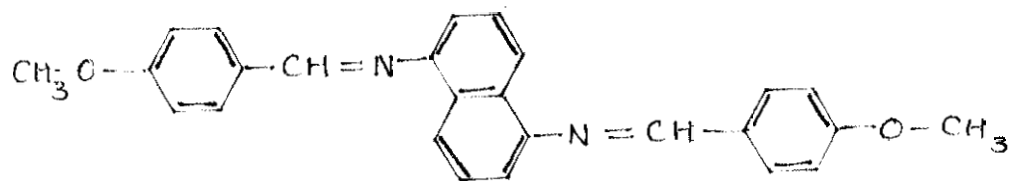
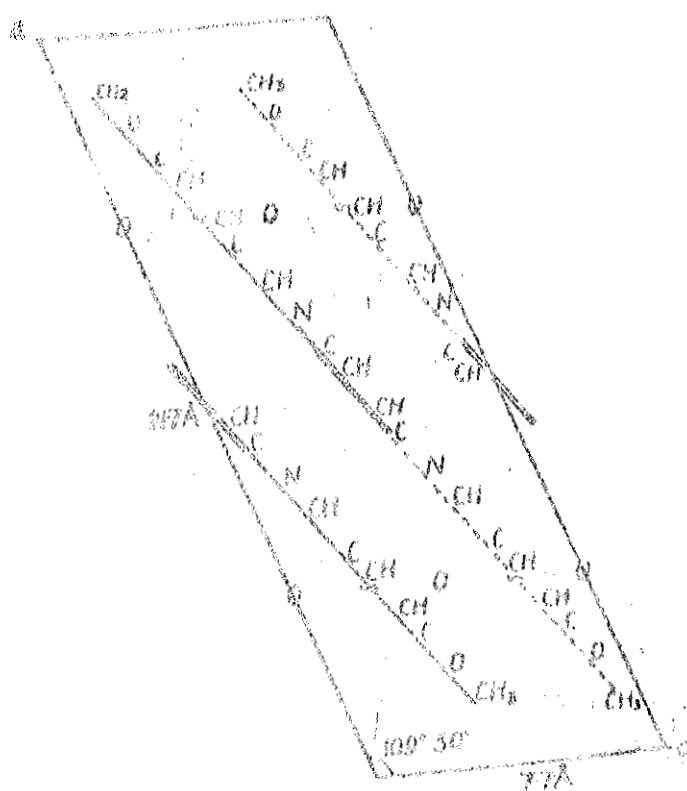


Figure 5.3: The molecular arrangement in the crystalline phase of *p*-azoxyphenetole as predicted by Bernal and Crowfoot [5].



(a)



(b)

Figure 5.4: The molecular arrangement in the stable solid phase of anisal 1:5 diaminonaphthalene as predicted by Bernal and Crowfoot [5].

the liquid crystalline phase. According to them, it is the molecular packing in the crystal structure of the higher metastable form which might hold in the liquid crystalline phase also.

(iv) Anisaldehyde-azine [10]. Fig. 5.5a & Fig. 5.5b.

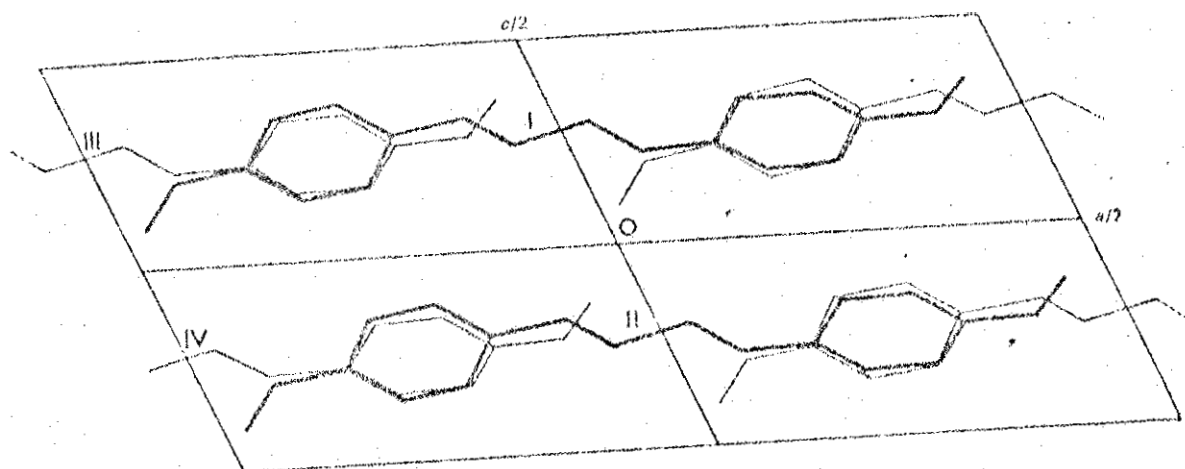
The molecular packing is imbricated so that the terminal active groups containing oxygen atoms have dipolar interactions with the atoms forming the double bonds in the central polarisable groups of the neighbouring molecules. The molecules pack with their axes more or less parallel to one another.

(v) 4-4' azodiphenetole [11,12]. Fig. 5.6

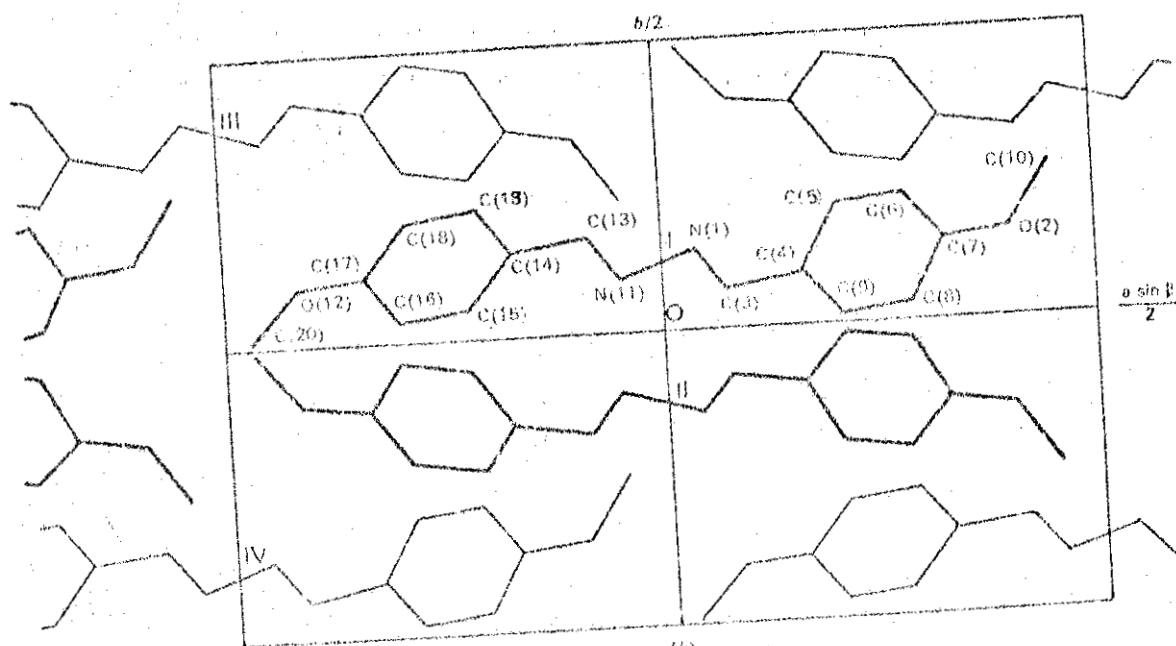
The molecules pack in an imbricated fashion, with their axes parallel to one another and the terminal active group of one molecule is in close proximity to the central polarisable group of its neighbour. Each molecule is surrounded by six neighbours, giving rise to a hexagonal type of packing.

(vi) p-methoxy cinnamic acid [13] Fig. 5.7, Fig. 5.8.

The molecules exist as hydrogen bonded dimers. The longitudinal axes of the dimers are all parallel and the dimers are stacked one above the other in a stepped fashion. The stepped stacks are repeated parallel to one



(a)



(b)

Figure 5.5: The molecular packing in the (a) *ac*-plane and (b) *ab*-plane of anisaldehyde-azine [10].

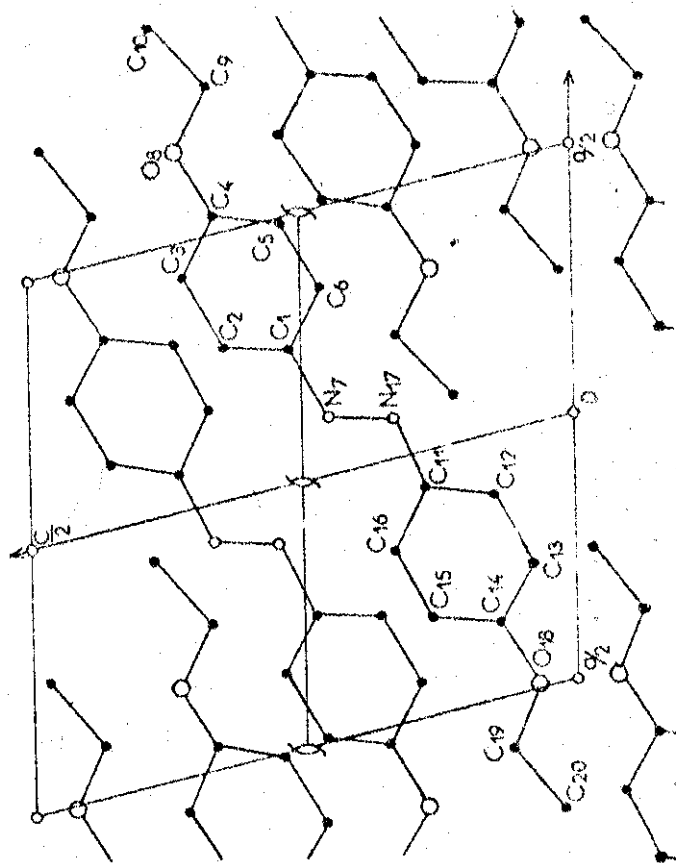


Figure 5.6: The molecular arrangement in the ac-plane in the crystal structure of 4-4' azodiphenetole [11].

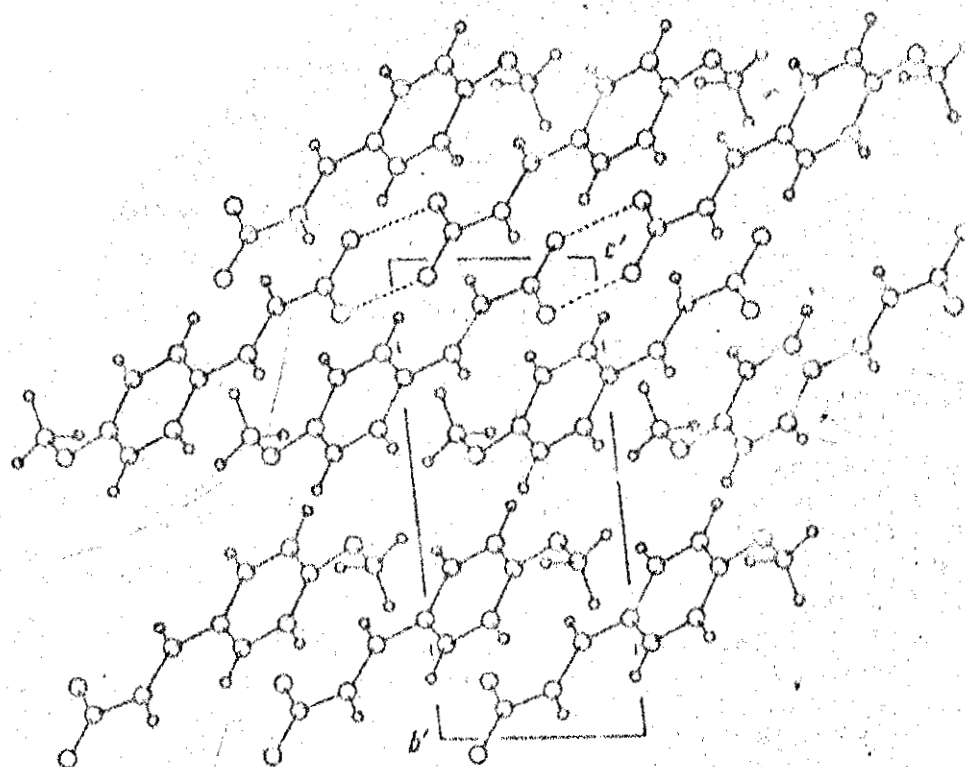
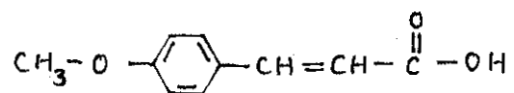
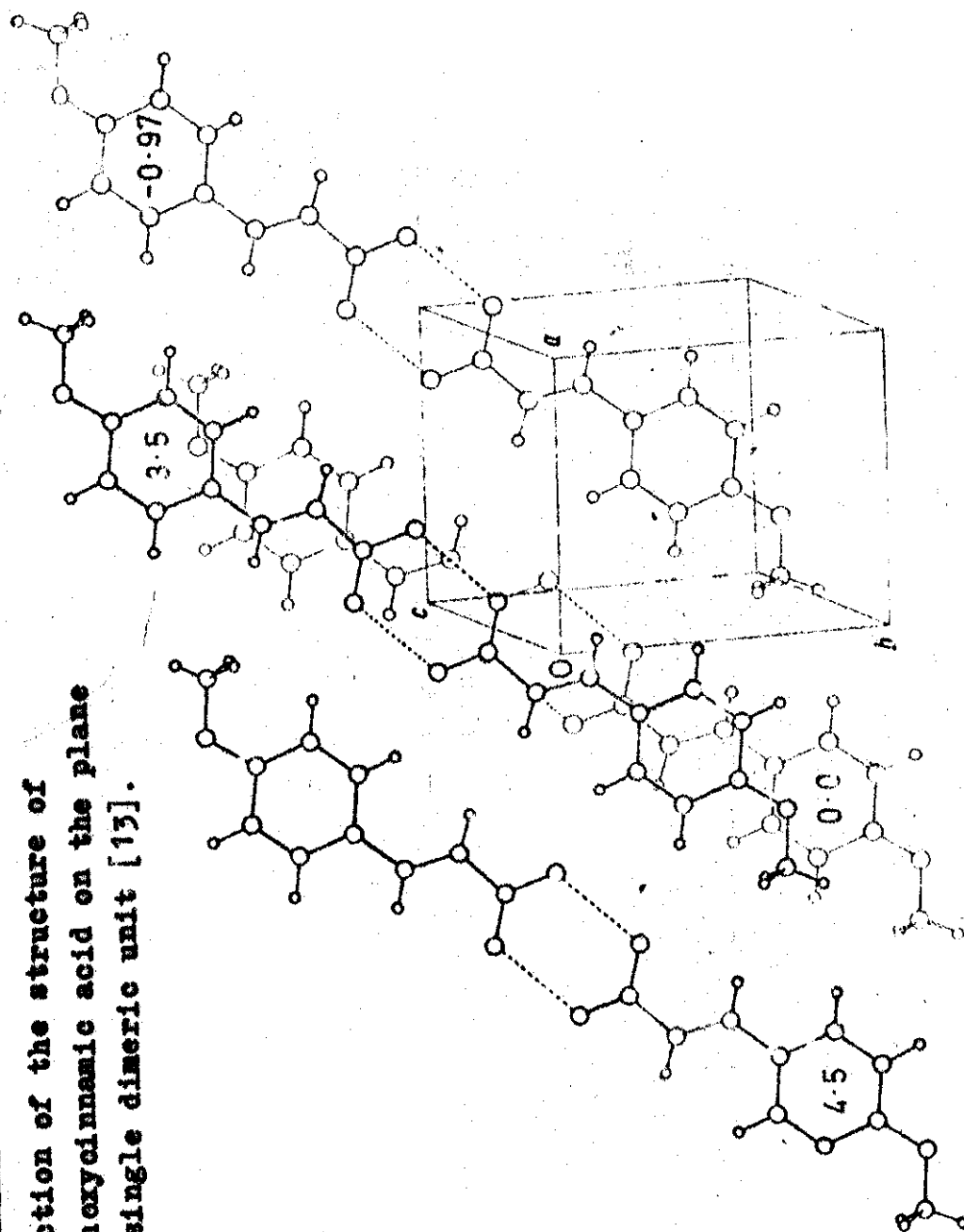


Figure 5.7: The molecular packing in the bc-plane of p-methoxycinnamic acid [13].

Figure 5.8

**Projection of the structure of
p-methoxycinnamic acid on the plane
of a single dimeric unit [13].**



another. The longitudinal displacement within a stack results in the carboxy-groups of one dimer being held between stereochemically rigid olefin groups of neighbours above and below. Also, due to the displacement between the stacks, the carboxy-linkages have the olefin groups and the phenyl rings as neighbours on either side. This type of imbricated molecular arrangement is found to be conducive to mesophase formation. In this arrangement, even if the hydrogen bonds rupture, the overlap of the neighbouring molecules persists to a considerable extent and the imbricated arrangement is retained.

The significance of imbrication of molecules in the mesophase formation is obvious when the crystal structure of *p*-methoxycinnamic acid is compared with that of α -*trans*-cinnamic acid [13] (Fig. 5.9 and Fig. 5.10). Cinnamic acid also exists as a hydrogen bonded dimer. Even though the molecules are geometrically anisotropic, the compound does not exhibit mesomorphism. The probable reason for this is that the parallel overlap between the dimers within a stack is much less in cinnamic acid, compared to *p*-methoxy cinnamic acid, leading to weaker intermolecular interactions within a stack. Also, unlike in the case of *p*-methoxy cinnamic acid, if the hydrogen bonds rupture, the imbrication of the molecules is lost. Therefore, the molecular arrangement does not appear to be conducive to the formation of mesophase.

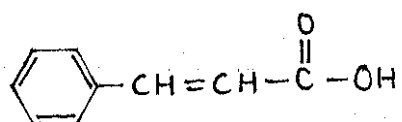
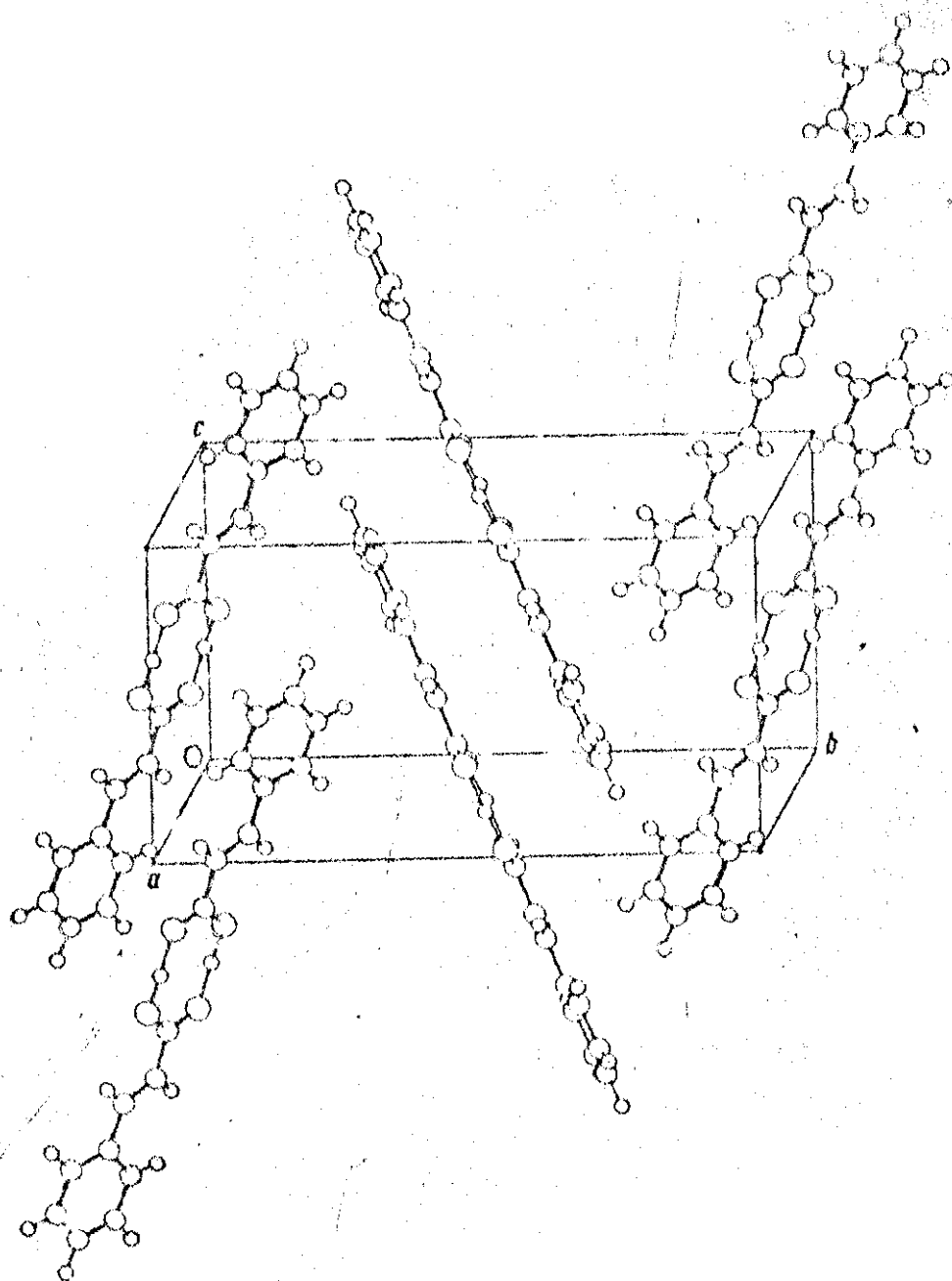


Figure 5.9: The molecular arrangement in the crystal structure of α -trans-cinnamic acid [13].

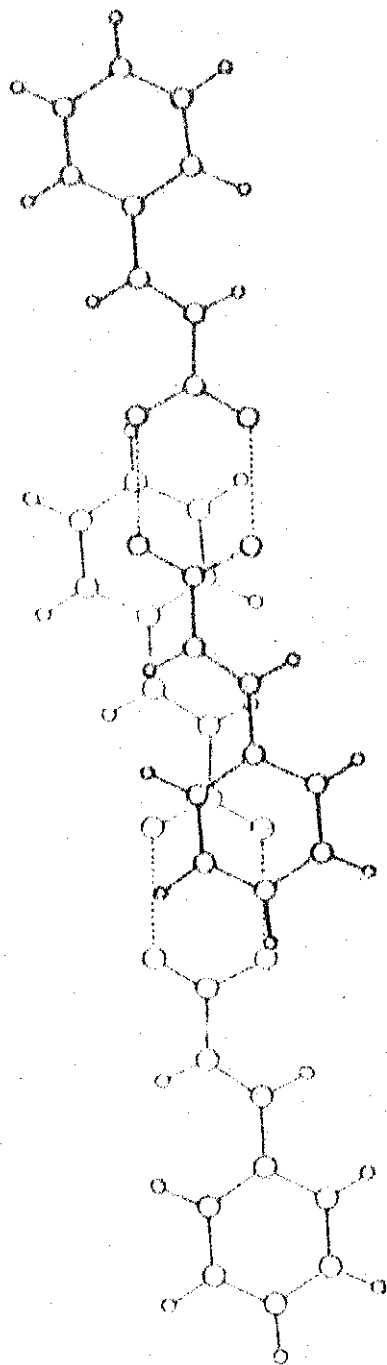


Figure 5.10: Projection on the molecular plane of a pair of centrosymmetrically related dimers of α -trans-cinnamic acid, illustrating the packing within a single stack [13].

The significance of the very critical nature of the intermolecular forces in the formation of mesophase could be appreciated further by comparing the molecular packing in the nematogen *p*-methoxy cinnamic acid with that in *p*-methoxy- and *p*-ethoxy benzoic acids [14,15], which are not mesogens. Unlike in *p*-methoxy cinnamic acid, the molecular arrangement in the latter two compounds is such that the phenyl ring of one molecule has phenyl rings of the adjacent molecules as neighbouring groups. This direct overlap between two phenyl rings results in a strong molecular interaction with high binding energy, which in turn leads to a high melting point for the compound. The strong interactions and the high binding energy values, thus, seem to inhibit mesophase formation.

The common features of crystal structures of all the nematogens mentioned so far are (i) imbricated arrangement of molecules, and (ii) the active end group of one molecule lying near the active group in the central part of a neighbouring molecule. In the nematogenic crystal structures described below, the packing of the molecules is slightly different.

(vii) Benzylidene aniline *p*-carboxylic acid [16]

Fig. 5.19

The molecules are arranged such that they are linked across the inversion centres into dimers by the

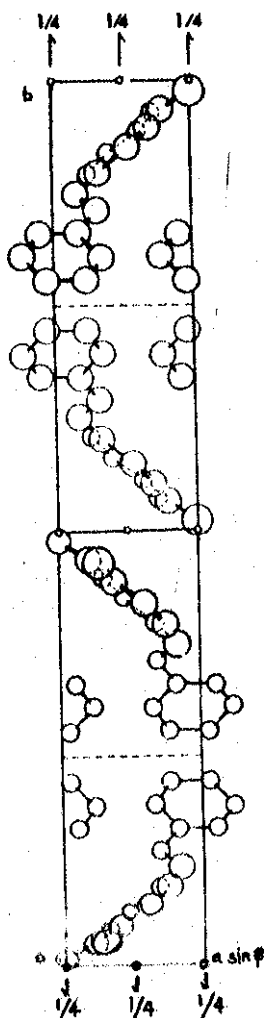
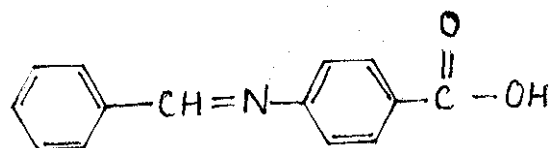


Figure 5.11: The molecular arrangement in the ab -plane of benzylidene aniline p-carboxylic acid [16].

formation of hydrogen bonds between carboxyl groups.

Unlike in the crystal structures described so far, the dimers in benzylidene aniline p-carboxylic acid are packed in a herringbone-like fashion.

(viii) 2,2'-dibromo-4-4'-bis-(p-methoxybenzylidene amino)biphenyl [17] Fig. 5.12.

This molecule can be divided into two halves at the biphenyl bond; however, the two halves are not identical crystallographically. The asymmetric unit consists of the 'half' portions of two different molecules. The molecules are packed in an imbricated arrangement in the crystal. The plane of one half of the molecule is nearly perpendicular to the plane of the other half. This, coupled with the imbrication of the molecules, causes each half portion of one molecule to be approximately perpendicular to the corresponding half portion of its neighbouring molecule. As a result, a herringbone-like packing of the benzene rings in planes perpendicular to the molecular axes is obtained.

(ix) N-p-methoxybenzylidene-p-phenylazoaniline (MBPAA).
Fig. 5.13.

A detailed account of the crystal structure analysis of this nematogen is given in chapter 2 of this thesis. For the sake of completeness, a brief mention of the molecular packing in this crystal is made here. The crystallographically

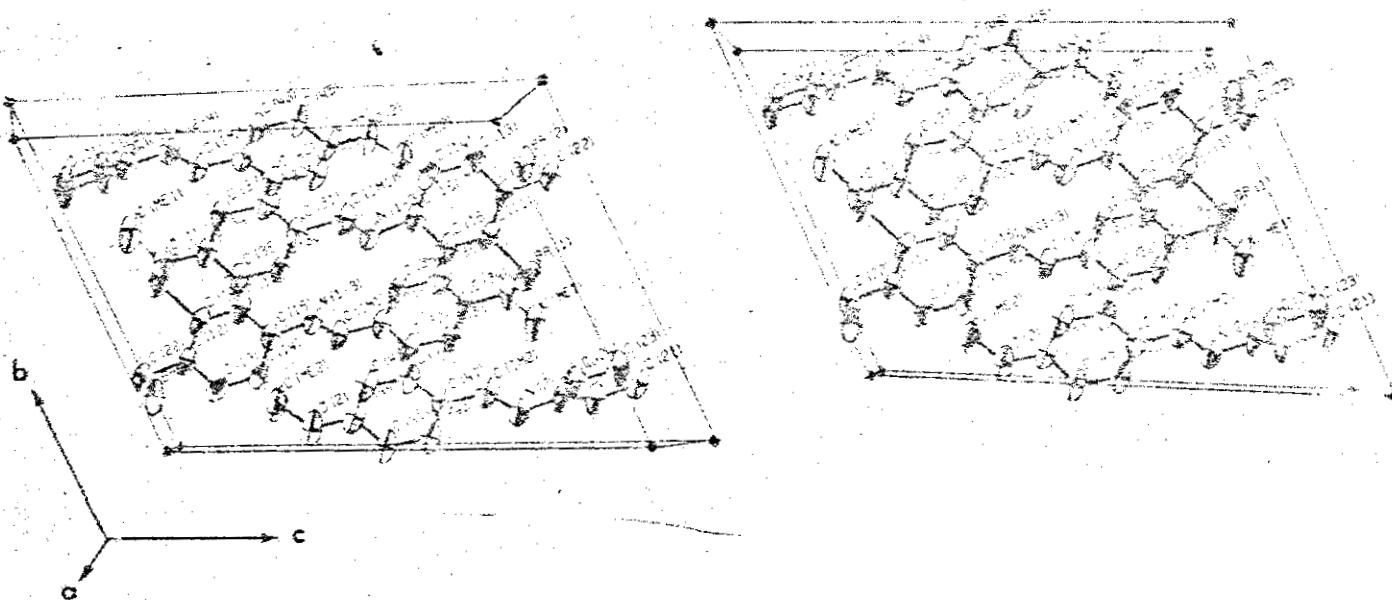
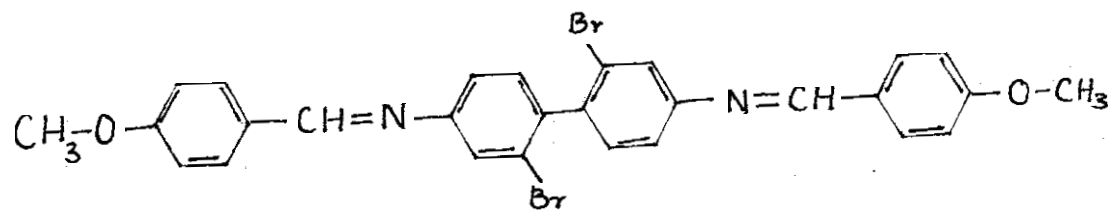


Figure 5.12: Steroscopic drawing of the unit cell of 2,2'-dibromo-4,4'-bis-(p-methoxy benzylideneamino)biphenyl [17].

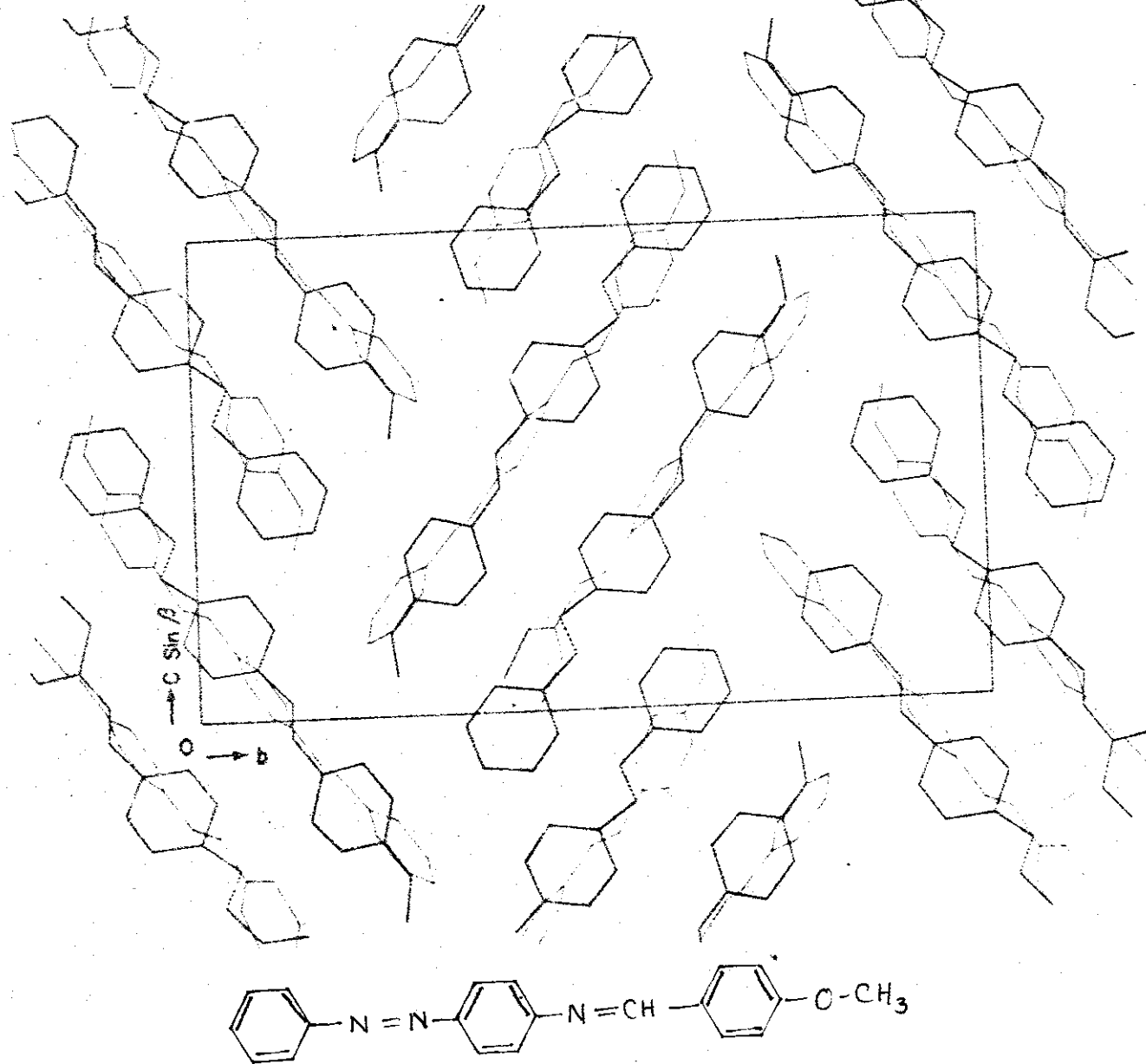


Figure 5.13: The packing of molecules in the bc -plane of n - p -methoxybenzylidene p -phenyl azoaniline [chapter 2].

independent molecules in the **unit** cell are **antiparallel** and lie almost exactly above each other in the bc-projection. To describe the packing of the **molecules**, the two **crystallographically** independent molecules and their symmetry **equivalents** generated by the centre of inversion at the origin, can be **considered as** one **unit**. This is indicated in Fig.5.13. These quadruple molecular units **are** arranged in an imbricated fashion and form an infinite column along the **c-axis**. The molecular **units** in adjacent **columns** are inclined to each other at about **70°**, leading to a herringbone-like pattern.

(x) Propyl 4-(4'-methoxybenzylidene amino)-**α**-methyl
cinnamate [18] i 5.14.

The molecular packing in the crystalline phase of this **nematogen** is considerably **different** from that in the **crystal** structures of the **nematogens** mentioned so far. The eight molecules in the unit cell are associated in pairs. A **dimer** formed by two **antiparallel** molecules related by an inversion centre, **comprises the basic structural** unit. These **dimer** units are **stacked** in a crossed **fashion**, resulting in a highly imbricated packing. In this structure, it is difficult to correlate the highly imbricated **packing** arrangement with the formation of the **nematic mesophase**. However, the authors suggest that the nematic **phase** may be formed **as** a consequence of the rupture of the interactions between the **dimers**, when the **dimer** unit itself **remains** Intact. **This** is possible because the interaction energy

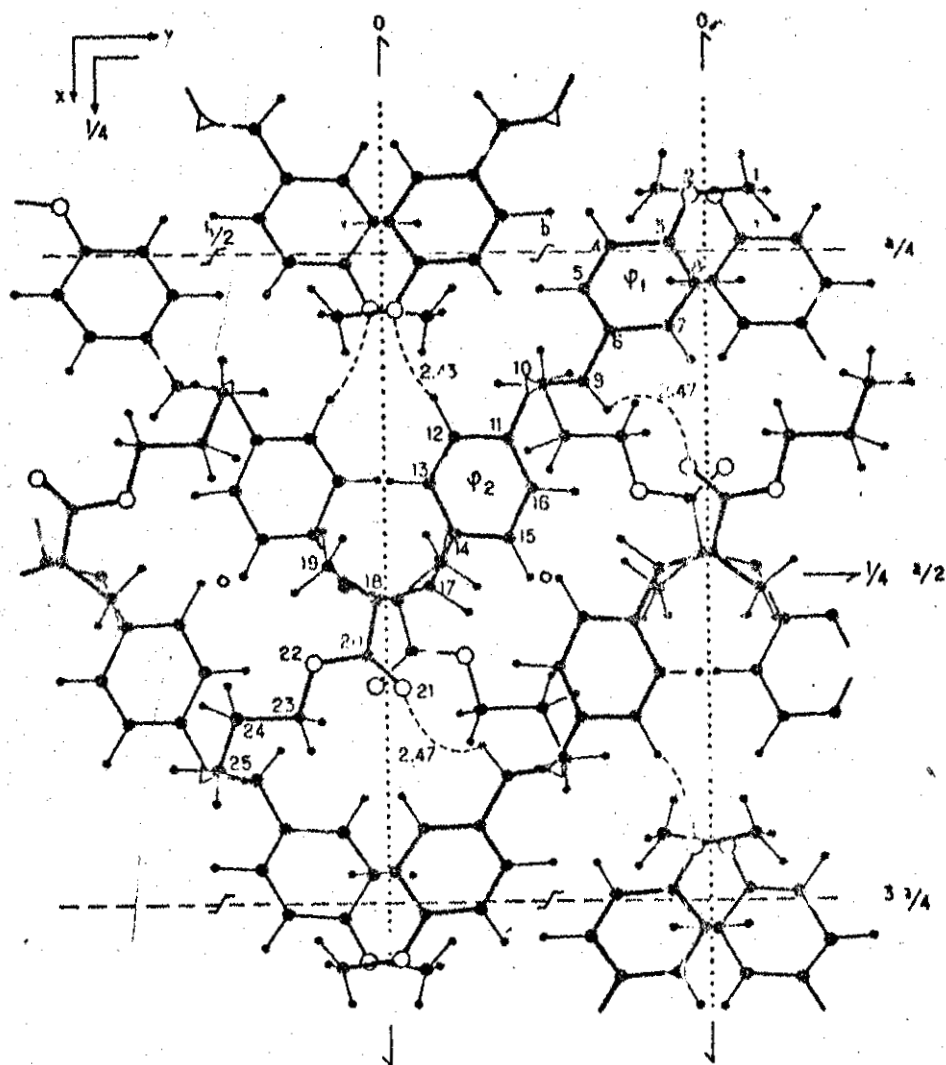
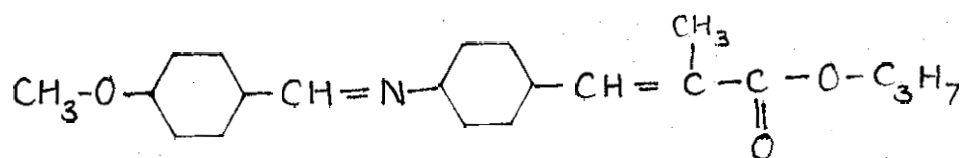


Figure 5.14: The molecular arrangement in the *ab*-plane of propyl 4-(4'-methoxy benzylideneamino)- α -methyl cinnamate [18].

between two **neighbouring** dimers is much **smaller** compared to the interaction energy between the two **antiparallel** molecules **which** form **the dimer**. The **rupture** of the **interactions** among the **dimers** would lead to a **local parallel** alignment of the **dimers**, resulting in an arrangement similar to that in a **nematic mesophase**. The authors **thus** predict that the **dimeric** unit **formed** by two antiparallel molecules persists in the **nematic** phase also.

(b) Smectogenic Crystall Structures.

As in the previous **section** on **nematogens**, the very early X-ray work on smectogens will be first referred to before describing in detail the results of the recent crystal structure analyses.

(1) Ethyl **anisal p-amino** cinnamata [5] Fig. 5.15.

Bernal and Crowfoot **predict** a layered structure for this crystal, with the **neighbouring** molecules within a layer having an **antiparallel** arrangement.

(11) Ethyl **p-azoxybenzoate** [19,20] Fig. 5.16 and Fig. 5.17.

This smectogen exists in two polymorphic **crystalline** modifications, referred to as solid I and solid II respectively. The crystal **structures** in both these phases have been determined. A layered **stacking** of **molecules**, characteristic of a smectogen is found in

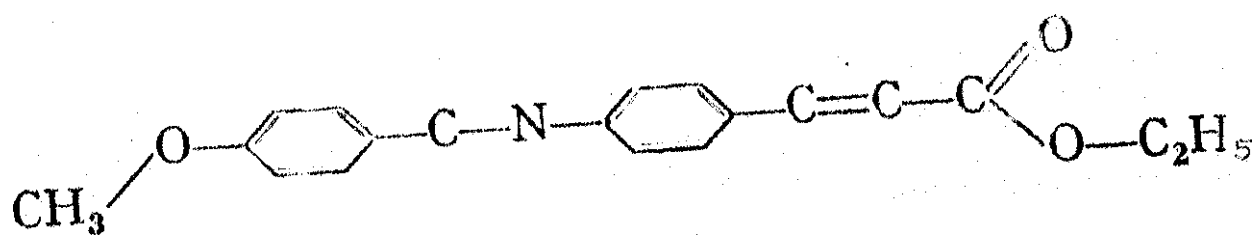


Figure 5.15

Ethyl anisal p-amino cinnamate

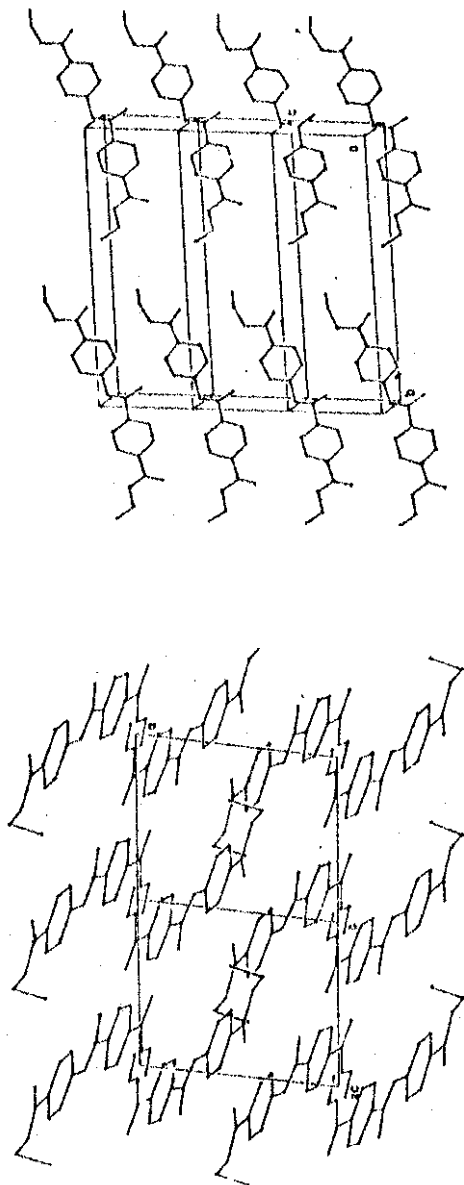
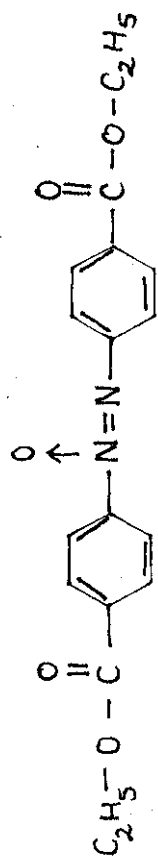


Figure 5.16: The molecular arrangement in the solid I phase of ethyl p-azoxybenzoate [19].

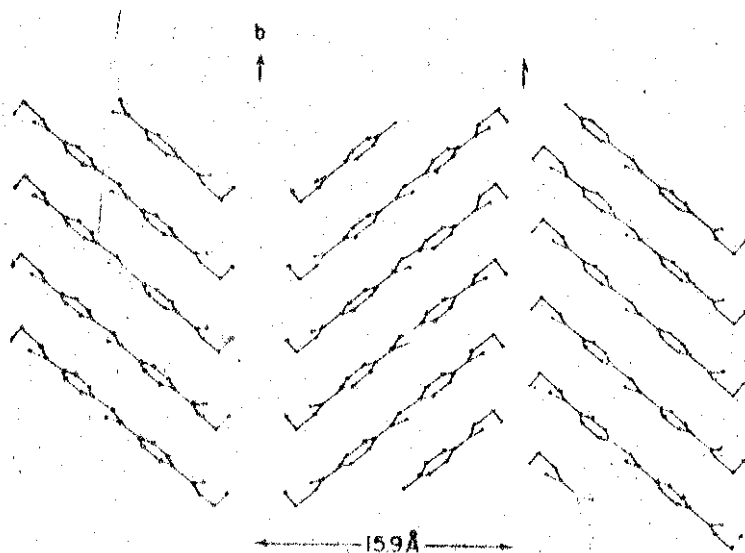
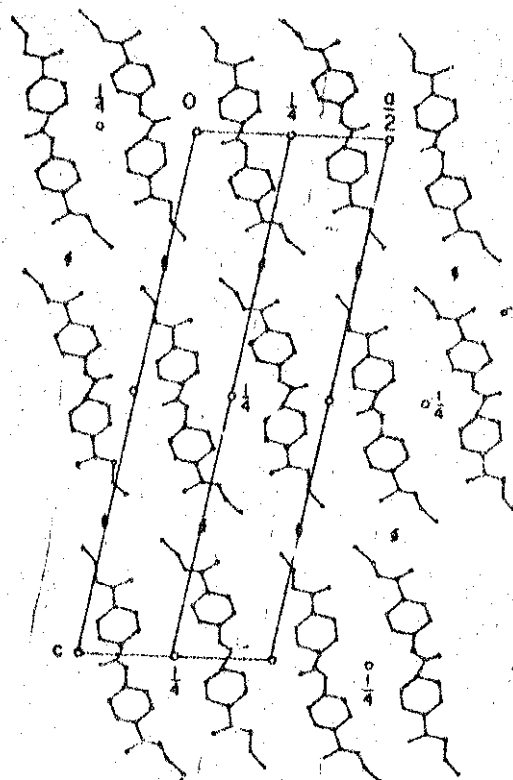


Figure 5.17: The molecular arrangement in the solid II phase of ethyl *p*-azoxybenzoate [20].

both the phases. Solid 11 has been found to be disordered, consisting of the trans-cis and the cis-trans conformers of the molecule in the unit cell. Of these, the former conformer is found to be more abundant. In contrast, solid I does not exhibit any disorder and consists only of the cis-cis conformer. In solid 11, the value of the component of the dipole moment perpendicular to the molecular axis and in the plane of the molecule is found to be less than half the value in solid I and the importance of dipolar interactions is found to reduce on going from solid I to solid II. Therefore, the authors feel that dipolar interactions are not likely to make a significant contribution to the lateral attractions between the molecules in the smectic phase, which follows the solid II phase.

(iii) (Methyl-2-butyl)-2(oxo-1-pentyl)-7 dihydro-9,10 phenanthrene [21] Fig. 5.18.

This smectogenic compound belongs to the acyl-alkyl dihydro phenanthrene series. In the crystal structure, the isopentyl chain of one of the two independent molecules is disordered and exists in two equiprobable positions. The nearest neighbours in the unit cell are oriented anti-parallel to each other and the molecules are stacked in layers.

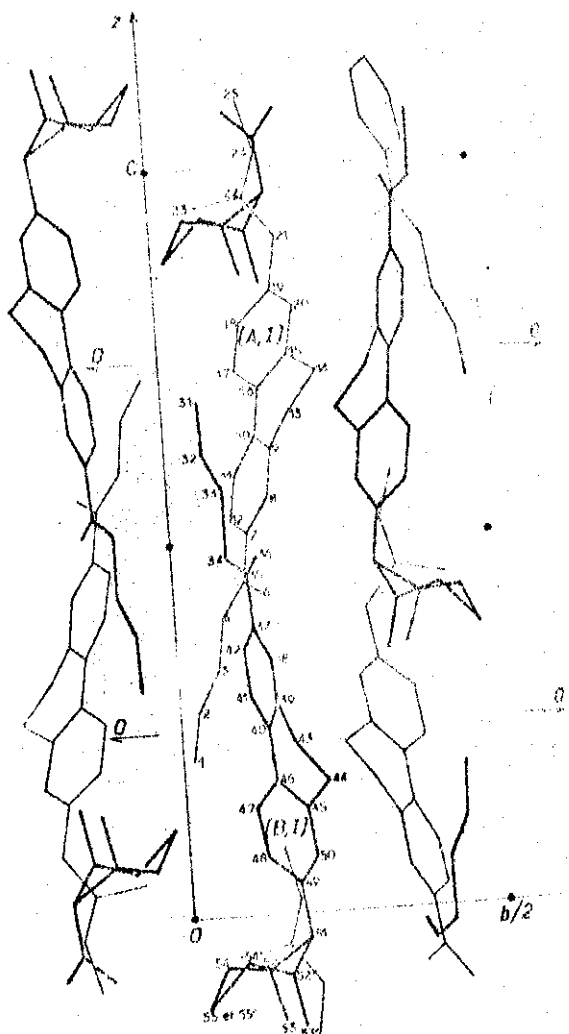
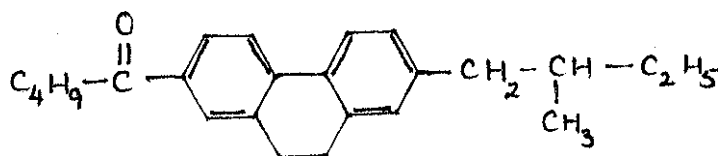


Figure 5.18

The molecular arrangement in the bc-plane of (Methyl-2-butyl)-2(oxo-1-pentyl)-7 dihydro-9,10 phenanthrene [21].

(iv) Butyl-2(oxo-1 pentyl)-7 dihydro-9,10 phenanthrene
[22] Fig. 5.19

This emeotogen also belongs to the acyl-alkyl dihydro phenanthrene series. The molecules in this crystal structure pack in layers and the molecules within a layer are associated in weak van der Waals interactions. The interactions are between the aliphatic side chains and the central rings, and between two aliphatic side chains of neighbouring molecules. The interactions between the adjacent layers are of the dipole-dipole type arising due to the interactions between neighbouring carbonyl groups. The nearest neighbours are antiparallel. The atoms in the aliphatic side chains on either side of the central aromatic group are characterised by very high thermal vibrations, but no specific mention of disorder has been made.

(v) Terephthal-bis-p-butyl aniline (TBBA) [23]
Fig. 5.20.

This compound exhibits two crystalline phases and several liquid crystalline phases. The crystal structure in the room temperature solid phase has been determined by Doucet et al [23]. The molecules pack in layers parallel to the bc-plane. The two butyl side chains of this molecule have been found to be disordered in the room temperature solid phase.

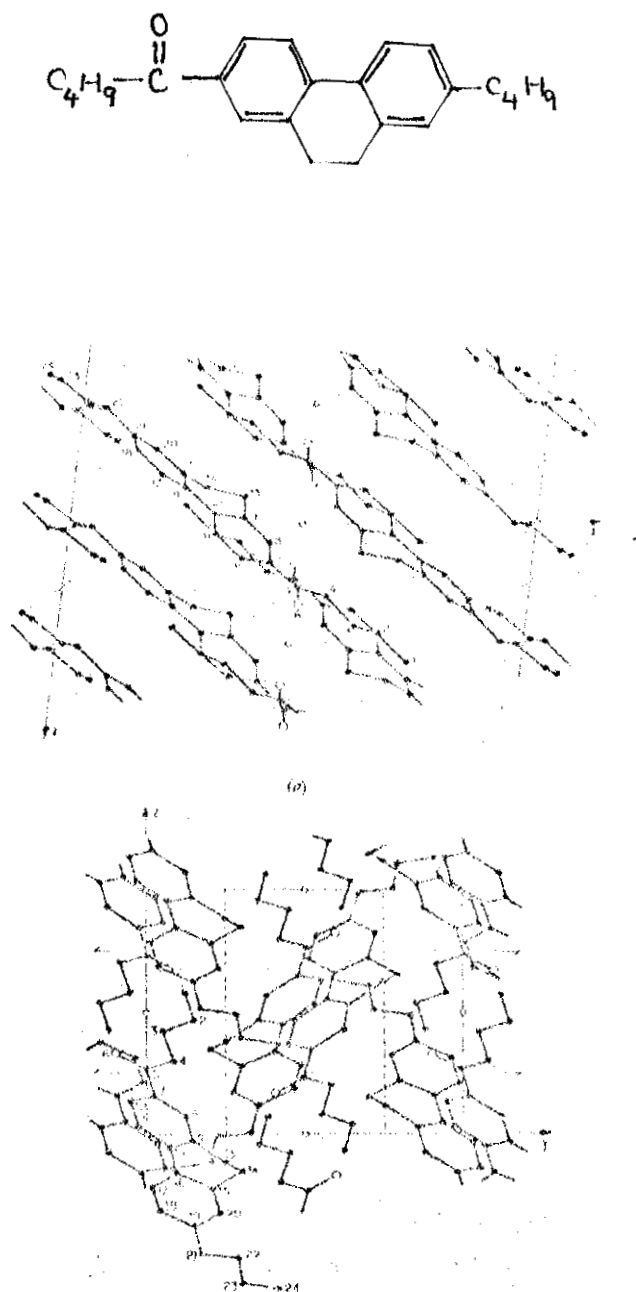


Figure 5.19

"The packing of molecules in the crystal structure of butyl-2(oxo-1-pentyl)-7 dihydro-9,10 phenanthrene [22].

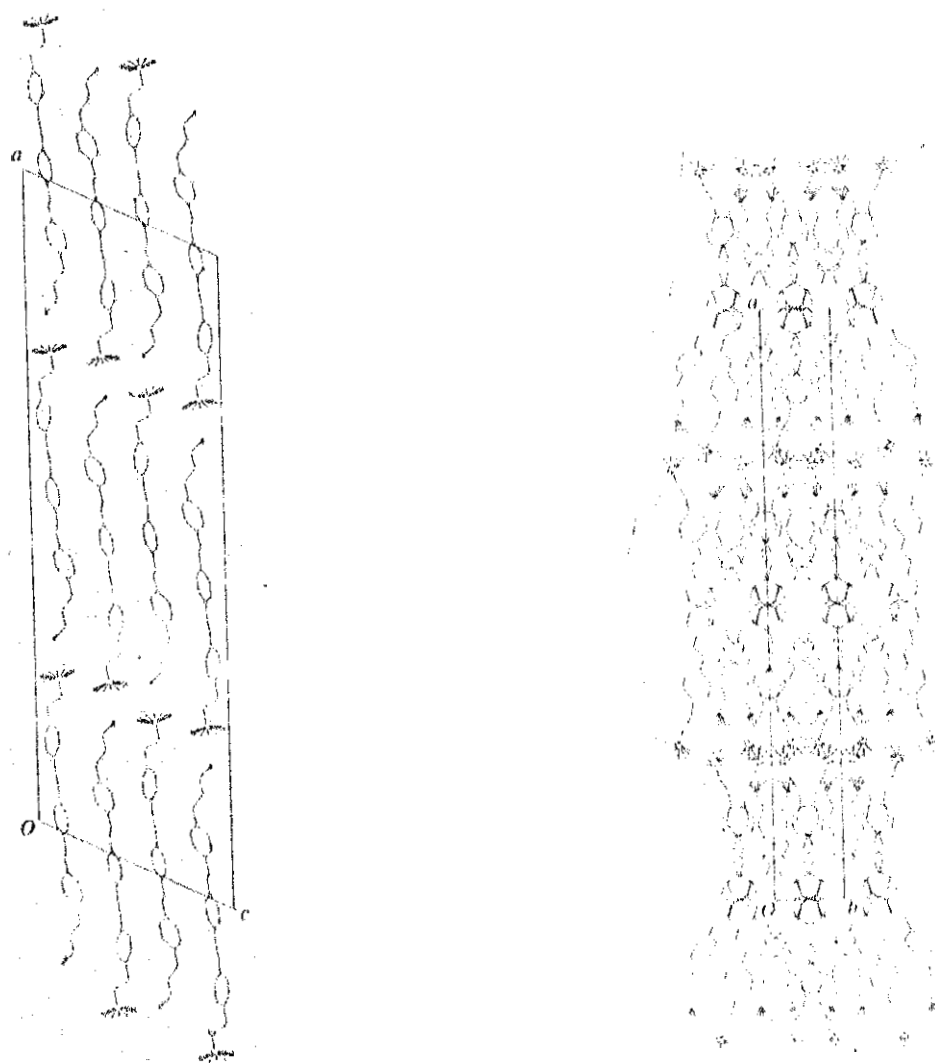
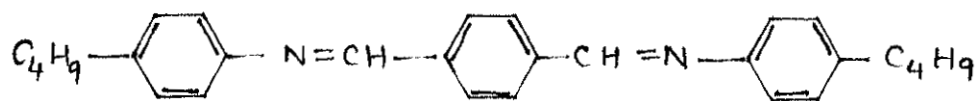


Figure 5.20

%**de molecular** arrangement in the crystal structure of terephthal-bis-*p*-butyl aniline [23].

(vi) **n-n-Cyanobenzylidene-n-n-octyloxyaniline (CBOOA).**
Fig. 5.21.

The crystal **structure** of CBOOA has been **analysed** by the author and a detailed account is given in Chapter 3 of this thesis. The **molecules** in this **crystal** are packed in **layers** parallel to the **ao-plane**. The arrangement of molecules in the **bc-plane** could be described as a **herringbone-like** pattern with the pairs of molecules related by an inversion **centre considered** as the basic repetitive unit. The nearest **neighbours** are oriented **antiparallel** to each other.

(vii) **Cholesteryl myristate [24] Fig. 5.22**

This **smectogen** exhibits a **cholesteric** phase intermediate between its **smectic** and **isotropic** phases. The molecular **packing** in the crystal corresponds to a layered **structure** expected of a smectogen. But unlike in the other **smectogenic** crystal **structures** discussed in this section, the molecules in **cholesteryl myristate** pack in **bilayers**. To describe this bilayer, a structural unit comprised of two **antiparallel cholesteryl myristate** molecules can be defined. These molecules are displaced longitudinally with **respect** to each other so that only their **myristate** chains **overlap**. The **thickness** of the bilayer is approximately equal to the effective length of this structural unit.

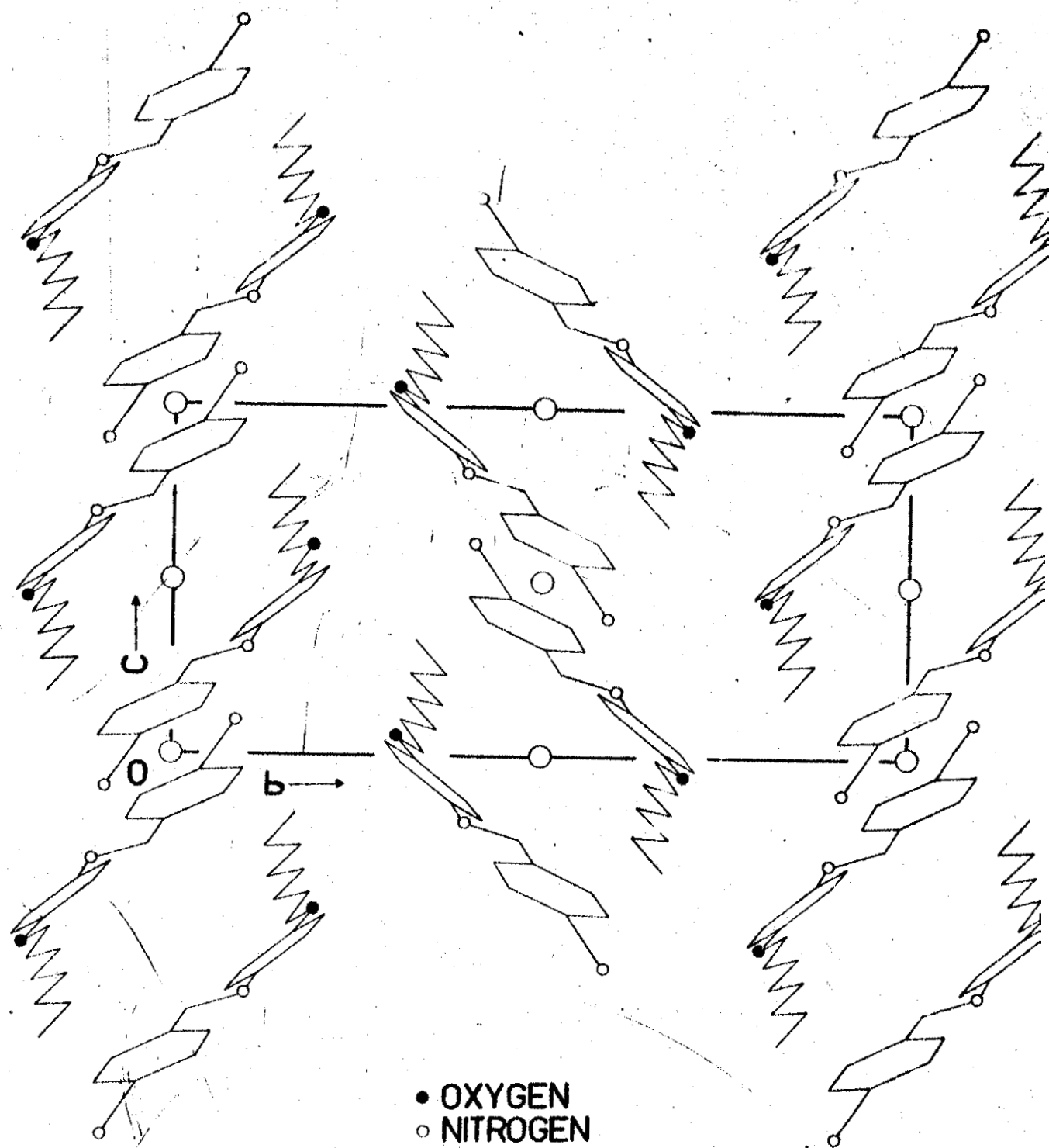
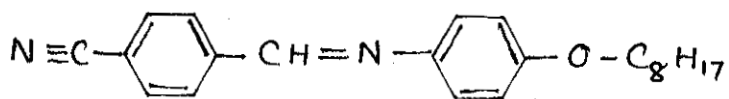


Figure 5.21

The arrangement of molecules in the bc-plane of CBOOA (chapter 3).

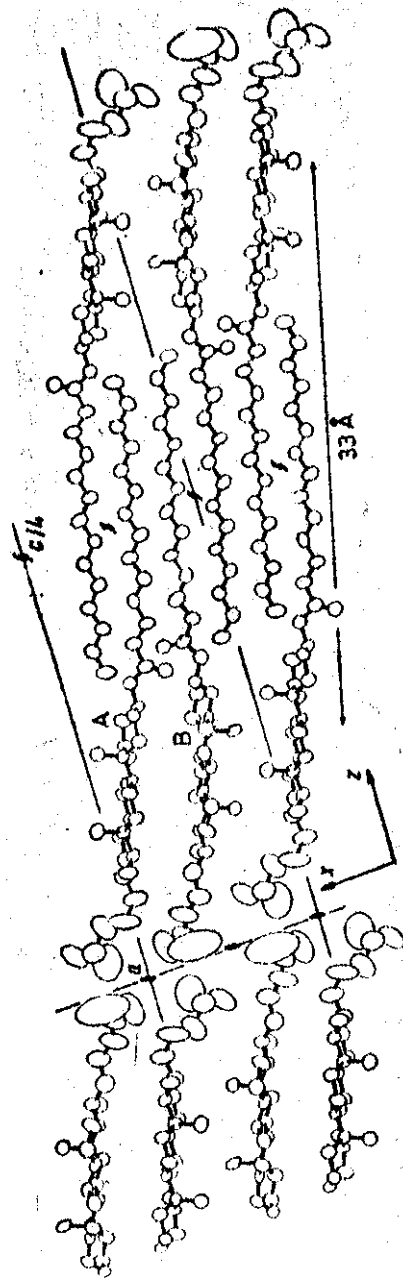
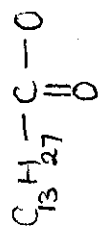


Figure 5.22: The molecular arrangement in the crystal structure of cholesteryl myristate [24].

The $O(17)$ side chains of both the crystallographically independent molecules of cholesteryl myristate are characterised by very high thermal parameters and are found to be disordered.

(c) Cholesterogenic Crystal Structures

Crystal structure of no liquid crystalline compound which transforms directly from the solid to the cholesteric phase has been reported. Cholesteryl myristate [24] whose crystal structure has been mentioned above in section 5.2(b), exhibits a smectic A phase intermediate between its solid and cholesteric phases and hence, the molecular packing in its crystalline phase resembles that in its smectic phase.

A detailed discussion on the crystal structures of cholesteryl chloride and the isomorphous cholesteryl bromide (Fig. 5.23) is given in Chapter 4 of this thesis. These are monotropic liquid crystals and exhibit the cholesteric mesophase only while cooling. Cholesterics being very similar to nematics, the molecular arrangement in a cholesterogen could be expected to be very similar to that in a nematogen. However, it is interesting to note that the molecules in these isomorphous cholesterogenic crystals pack in layers in a smectic-like fashion. The crystal structures are characterised by very high thermal

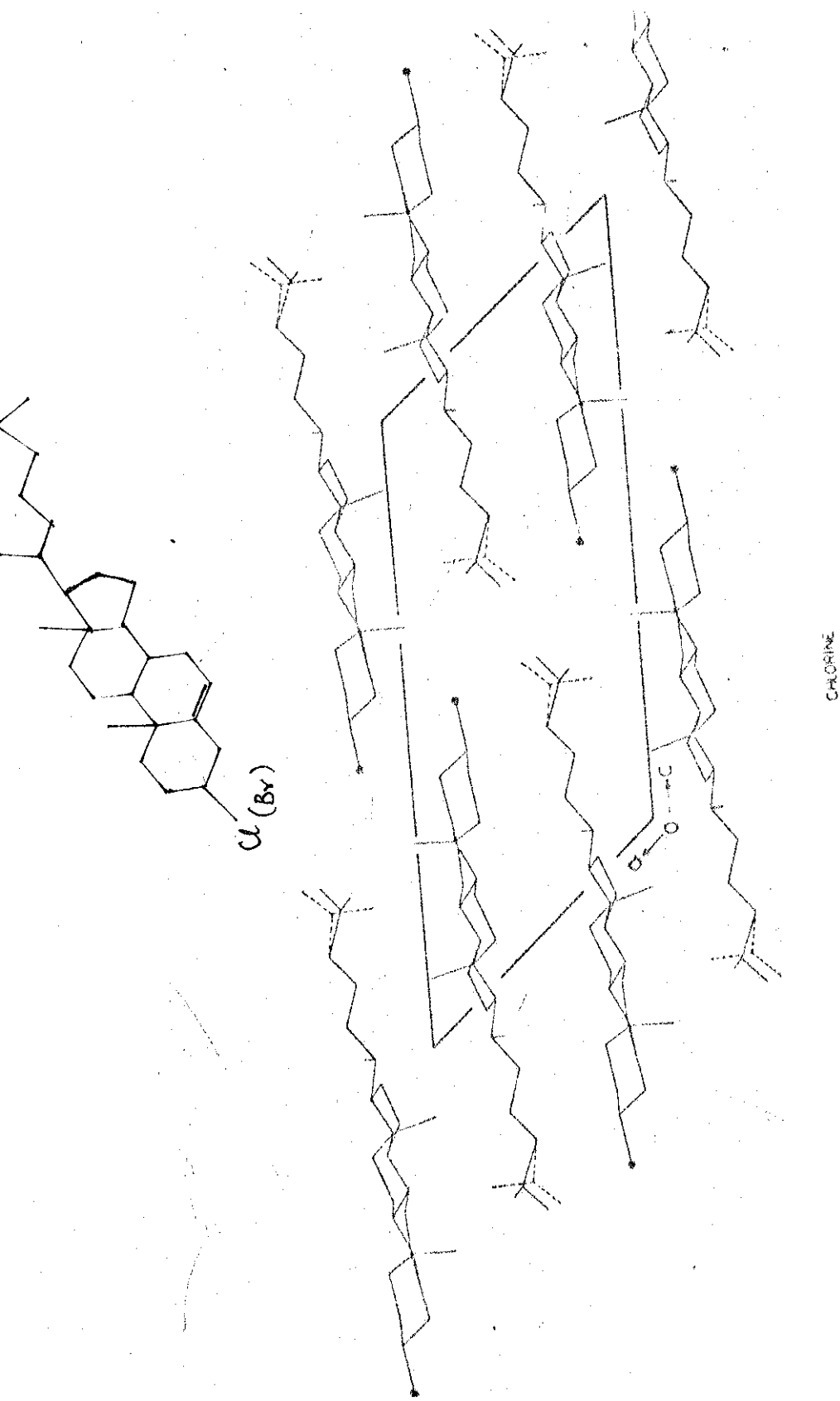


Figure 5.23: The molecular arrangement in the ac-plane of cholesterol chloride (bromide) (chapter 4).

parameters and the end chain is found to be disordered.

53 Characteristics of mesogenic crystal structures

The above survey of the mesogenic crystal structures confirms the observations of Bernal and Crowfoot [5] that nematogens generally have an imbricated molecular packing, as contrasted with the layered arrangement found in smectogens. Among the smectogenic crystal structures discussed above, (methyl-2-butyl)-2(oxo-1-pentyl)-7 dihydro-9,10 phenanthrene [21] and ethyl-p-azoxybenzoate [19,20] transform directly into the isotropic phase from the smectic mesophase whereas, the others exhibit an intermediate nematic or cholesterio mesophase also. But there is no distinct difference in the molecular packing in these two types of compounds in their respective crystalline phases. The layer-like packing in the cryetalline phase of all these compounds resembles that in the smectic phase which Immediately follows, and does not seem to be affected by the phases following the smectic phase.

The intermolecular cohesive forces among the polarisable groups of neighbouring molecules generally results in a parallel (or antiparallel) arrangement of molecules in a mesogen. The strength of those forces is determined mainly by the type of polarisable groups present and their relative positioning and this, in turn, is

reflected in the arrangement of molecules in the **crystal structure**. Thus, the presence and positioning of **polarisable** groups, the **intermolecular** forces and the molecular **arrangement** in the **crystal** are **interdependent** and jointly determine the mesogenic *or* non-mesogenic nature of a compound **consisting** of geometrically anisotropic molecules.

When the molecules are geometrically anisotropic, a **crystal** lattice having a **layered** molecular arrangement is likely to form a **smectic mesophase** if the lateral forces between the molecules are strong and the terminal forces are weak. If **these** lateral **cohesions** are strong enough, they may **persist** until the isotropic phase **is** reached whereas weaker lateral attractions may lead to the formation of a **nematic** mesophase intermediate between the **smectic** and the isotropic phases. On the other hand, if the cohesive forces are too strong, the crystalline phase **may** transform directly into the isotropic phase. A similar line of argument is also true for a **crystal** with an **imbricated** molecular arrangement.

However, based on **the** present day **understanding** of the **intermolecular forces**, it is difficult to predict whether a **compound** will form a liquid crystal on heating *or* the type of **mesophase** it will exhibit, even **when** the molecular packing **in** the crystal is known.

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