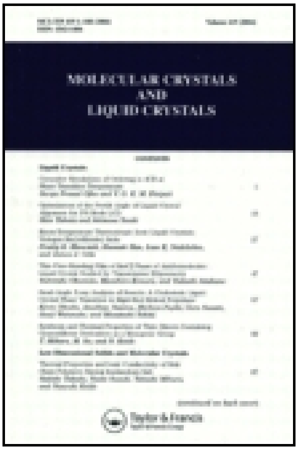

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

X-Ray Photographic Studies of Liquid Crystals: II. Apparent Molecular Length and Thickness in Three Phases of Ethyl-p-ethoxybenzal-p-aminobenzoate

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Version of record first published: 28 Mar 2007.

To cite this article: Adriaan De Vries (1970): X-Ray Photographic Studies of Liquid Crystals: II. Apparent Molecular Length and Thickness in Three Phases of Ethyl-p-ethoxybenzal-p-aminobenzoate, Molecular Crystals and Liquid Crystals, 11:4, 361-383

To link to this article: http://dx.doi.org/10.1080/15421407008083528

Molecular Crystals and Liquid Crystals. 1970. Vol. 11, pp. 361–383
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X-Ray Photographic Studies of Liquid Crystals†

II. Apparent Molecular Length and Thickness in Three Phases of Ethyl-*p*-ethoxybenzal-*p*-aminobenzoate‡

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Received July 29, 1970

Abstract—A general theory is developed for the relation between the molecular length and the position of a diffraction maximum found at diffraction angles of the order of 4°, for nematic and isotropic phases containing elongated molecules. Using this theory and a previously developed one for the relation between the intermolecular distance and the position of the major diffraction maximum at larger diffraction angles, molecular parameters are determined for three phases of ethyl-*p*-ethoxybenzal-*p*-aminobenzoate. These parameters are: the thickness of the smectic layers (19.941 Å), the length of the molecules in the isotropic phase (21.4 Å), and the intermolecular distances in the smectic (4.894 Å), nematic (4.932–4.950 Å), and isotropic phases (4.950–5.182 Å), all as a function of temperature. From these data, densities and volume expansion coefficients are calculated which agree very well with literature data on similar compounds.

There appears to be no room for rotation of the molecules around their long axes, not even in the isotropic phase. In the isotropic liquid the experimentally determined molecular length is very close to the calculated length of the stretched molecule (21.6 Å), but the thickness of the smectic layers is significantly less than this. The angle between the long molecular axes and the smectic planes (in the smectic A phase) is found to be very close to 90°. The nematic phase' appears to be a classical nematic phase: there is no significant ordering of the molecules apart from the near parallelism of the long axes of neighboring molecules.

The transition temperatures found are: C—L = 93.4 °C; N—L = 87.6 °C; S—N = 80.4 °C.

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† Research supported by contract F44620–69–C–0021 monitored by the Air Force Office of Scientific Research.

‡ Paper presented at the Third International Liquid Crystal Conference Berlin, West Germany, August 1970.

1. Introduction

The work reported is part of an ongoing program for the quantitative determination of molecular parameters in liquid crystalline phases. This program was undertaken because we feel that the determination of these molecular parameters (the apparent molecular length and thickness) for a number of compounds will enable us to draw valuable conclusions with regard to the molecular packing in liquid crystals and in the related isotropic liquid phases. The results obtained so far are encouraging; in the first paper in this series(1) we showed that there are at least two different types of nematic phases (the classical nematic phase and the cybotactic nematic phase), and we were able to present a model for the molecular arrangement in the cybotactic nematic phase. In this paper some conclusions will be drawn with regard to the molecular packing in the smectic A phase(2) and in the classical nematic phase. As more compounds will be investigated, we expect to be able to draw further conclusions and to confirm the earlier ones.

Since little work has been done so far in this area, we had to develop some new theories and formulas for the interpretation of the X-ray diffraction effects encountered in the study of liquid crystals. In the previous publication(1) we showed that there was a diffraction ring (called the " inner ring ") related to the length of the molecules, and a diffraction ring (called the " outer ring ") caused by the interaction of neighboring, parallel molecules. A theory was developed for the inner diffraction ring of cybotactic nematic phases, and a general theory was worked out for the diffuse outer diffraction ring of smectic, nematic, and isotropic phases. We also gave the formula which should be used in calculating the intermolecular distance from the diameter of the outer ring. This paper presents a general theory for the relation between the position of the inner diffraction ring and the length of the molecules in classical nematic and isotropic liquid phases containing elongated molecules; we also will report numerical data on a specific compound.

This compound, ethyl-*p*-ethoxybenzal-*p*-aminobenzoate (EEB for short), $C_2H_5O{\cdot}C_6H_4{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}COOC_2H_5$, was selected for several reasons. It had a smectic A and a nematic phase, a combination that we wished to study (we reported earlier(1) on nematic phases related to smectic C phases). The molecule is short; this means that the inner diffraction ring occurs at larger diffraction angles and thus can be measured more accurately. The molecule is relatively rigid; this facilitates the interpretation of the results. The transition temperatures are fairly low; this reduces the chance for decomposition of the material during the measurements.

The data reported in this paper are the thickness of the smectic layers, the length of the molecules in the isotropic phase, and the intermolecular distances in the smectic, nematic and isotropic phases, all as a function of temperature. From these data we calculated volume expansion coefficients and densities for the various phases, and we compared these calculated values with data from the literature. The agreement appears to be very good.

Since there was some disagreement between the transition temperatures obtained from various sources, we also made careful measurements of these temperatures.

2. Experimental Procedures

X-ray diffraction patterns from samples in glass capillaries (0.5 and 1.0 mm diameter) were recorded on flat pieces of film with the camera described earlier,⁽¹⁾ using Ni-filtered Cu radiation. The same setup was also used for the determination of the transition temperatures. Relative values for these temperatures were obtained from the thermometer in the thermostat which circulated oil through the copper block which held the capillaries. Subsequently, this thermometer was calibrated using capillaries with melting point standards†; the calibration points were reproducible to within 0.1 °C from their mean values.

To determine the diameters of the diffraction rings we used the following procedures. For the reflections from the smectic layers (which are *sharp* reflections) we measured the diameter of the second order diffraction ring (the highest order clearly visible on the photographs) with a ruler, directly on the film. The diameters for all the other, more diffuse, maxima were determined by scanning the films on a densitometer (a Siemens recording photometer), recording the

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† These standard substances were obtained from the Mettler Instrument Corporation.

density patterns on charts and measuring these charts with the same ruler used for the measurements of the smectic inner rings. For these measurements the position of a maximum was defined as the point of intersection of the two straight lines drawn through the practically straight upper portions of the slopes on either side of the maximum.

To calibrate the diameters thus obtained, we also measured the diameter of the 111 reflection of aluminum (lattice spacing 2.3284 Å), using capillaries filled with aluminum powder.

For the calculation of the intermolecular distance D (in this paper we shall always take this to mean the average distance between the long axes of neighboring parallel molecules) from the diameter of the outer diffraction ring (the main diffuse diffraction maximum in photographs from smectic, nematic and isotropic phases), we shall always use here the formula(1) $2D \sin\theta = 1.117\lambda$, where θ is one half of the angle between the incident X-ray beam and the diffracted beam (calculated from the diameter of the diffraction ring and the sample-to-film distance) and λ is the wavelength of the radiation (1.5418 Å for our measurements).

3. Results

In the discussion of the X-ray data in this section, special attention has been given to the alignment condition of the samples. This has been done because the alignment has considerable influence on the accuracy of the measurement and upon what measurements can be made, and because it is possible that the packing of the molecules might be slightly different in well-aligned regions as compared to regions with random orientation, e.g., in a well-aligned region the intermolecular distance might be shorter. We have found no convincing evidence for this in our results, but nevertheless it seemed advisable to record the state of alignment of the samples.

The results obtained from the X-ray measurements have all been presented in the form of graphs, and where appropriate the best straight line through the data points has been calculated with the method of least-squares. There is, of course, no real reason why the relationships presented in the graphs would have to be given by straight lines, but our data gave no indications that other curves should be used.

THE TRANSITION TEMPERATURES

Transition temperatures for the crystal-isotropic liquid point (C—L), the nematic–isotropic liquid point (N—L), and the smectic–nematic point (S—N) have been reported in the literature⁽²⁾ and also had been determined in our Institute by various methods (see Table 1, columns 1–5). Since these data did not agree too well, and also since a question was raised concerning the existence of a second smectic phase at lower temperatures,⁽³⁾ we decided to determine these transition temperatures as accurately as possible using the heating system from the X-ray camera and observing the sample through a low-powered microscope. This method had the advantage of allowing one to keep the sample for extended periods of time at any given temperature (constant to less than 0.1 °C); thus, the speed of the transition, which is sometimes slow, is of no influence. The reproducibility of the measurements was very good; the transition temperatures were always within 0.1° from their mean values.

TABLE 1 Transition Temperatures in °C

	1	2	3	4	5	6	7
C—L	92.1	94.2	93.8	92.5	92.0	93.0	93.4
N—L	82.4	85.3	84.1	86.6	87.2	87.2	87.6
S—N	77.7	77.4	76.5	79.0	80.1	80.0	80.4

The origins of the various sets of data are: (1) Demus and Sackmann⁽²⁾; (2), (3) microscopic observations on two different batches; (4) DTA (differential thermal analysis) from the same material as used for (2); (5) DTA results from zone-refined material; (6) X-ray-oven data from the same material as used for (2) and (4); (7) X-ray-oven data from the same material as used for (5).

The values thus obtained (Table 1, columns 6 and 7) differ considerably (up to 5 °C) from the literature data (column 1) and from the microscope data (columns 2 and 3). The differences with the DTA data (columns 4 and 5) are of the order of 1°. Zone refinement of the material resulted in raising all transition temperatures by 0.4° (columns 6 and 7). We also found that the N—L and C—L temperatures of the zone-refined material went down fairly rapidly toward those of the not zone-refined material if the material was kept at temperatures above the C—L point, and also that the C—L temperature of a sample of the not zone-refined material decreased by about 0.25° in the course of time.

The values in column 7 of Table 1 appear to us to be the most reliable ones; they are the ones used in the following schematic phase diagram of EEB:

$$\begin{tikzcd}
\text{Solid} \arrow[r, leftrightarrow, "93.4^\circ"] & \text{Isotropic liquid} \arrow[d, leftrightarrow, "87.6^\circ"] \\
\text{Smectic} \arrow[u, "(\text{ca. } 70^\circ)"] \arrow[r, leftrightarrow, "80.4^\circ"] & \text{Nematic}
\end{tikzcd}$$

As far as the possible existence of a second smectic phase at lower temperature is concerned, our photographs did not show any change in the diffraction pattern down to 70 °C, and our measurements (Figs. 1 and 2) do not indicate any significant change in the molecular parameters down to 72 °C. So if there is a second smectic phase, it is very unlikely that it exists above 72 °C.

THE SMECTIC PHASE

In the discussion of the X-ray diffraction photographs of the smectic phase we shall distinguish between the *inner* diffraction maxima, which are caused by the smectic layer arrangement (we usually observed the first and the second order of this reflection against the smectic planes), and the *outer* diffraction maxima, which are caused by the interaction between neighboring parallel molecules.(1) There are other, less pronounced, diffraction effects visible on the photographs, but they will not be discussed in the present paper.

In this section, and in the following ones, we shall first discuss the outer diffraction maxima and next the inner diffraction maxima. All photographs of the smectic phase of samples in 0.5 mm capillaries indicated a strong alignment of the long molecular axes approximately parallel to the direction of the capillary axis (the one photograph made using a 1.0 mm capillary showed much less alignment). The planes of the smectic layers appeared to be perpendicular to the direction of the long molecular axes, and thus approximately perpendicular to the walls of the capillary. This behavior is in agreement with microscopic studies, in which pseudoisotropic textures were not or seldom observed for this compound.[2]

Because of this strong alignment the two maxima in the outer diffraction ring were very strong and extended only over a limited area on the photograph. Measurements of the diameter of the outer diffraction ring were, therefore, accurate in the direction of these maxima (which are situated diametrically opposite each other when the molecular axes are perpendicular to the incident beam) or in directions close to the direction of the maxima, but measurements in other directions could not be made. From each photograph two or more measurements were made, and from the average for each photograph we calculated the corresponding intermolecular distance D. These distances are plotted in Fig. 1. They comprise the results from seven series of photographs, obtained from four different capillaries using three slightly different sample-to-film distances (caused by small changes in the setup). The agreement between the measurements is seen to be quite good. A least-squares analysis of the data indicated that the best straight line through the set of data points (the line drawn in Fig. 1) had a slight positive slope of 0.0009 Å/degree, with a standard deviation σ of 0.001 Å/degree. The standard deviation σ for the individual data points was 0.01 Å.

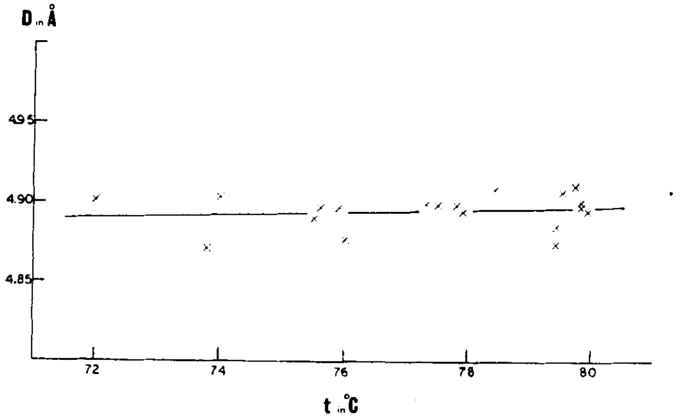

Figure. 1. The intermolecular distance in the smectic phase as a function of temperature.

For the measurement of the diameter of the inner ring the same set of photographs was used, plus one photograph taken at only 0.2 °C below the S—N point (the outer maxima were not measured on this photograph because the exposure time had been so much shorter than usual that the outer maxima were not well enough developed). The strong alignment of the molecules again limited the directions in which the diameter of the inner ring could be measured, and sometimes we could make only one measurement per film.

The sharpness of the inner ring maxima indicated that they were caused by regular arrangements of large numbers of smectic layers parallel to each other. For the calculation of the corresponding lattice distance d (the " thickness " of one smectic layer) we used, therefore, the regular Bragg equation $2d \sin\theta = n\lambda$, where n is the order of the reflection ($n = 2$ for our measurements). Values of d for each photograph are plotted in Fig. 2; the agreement between

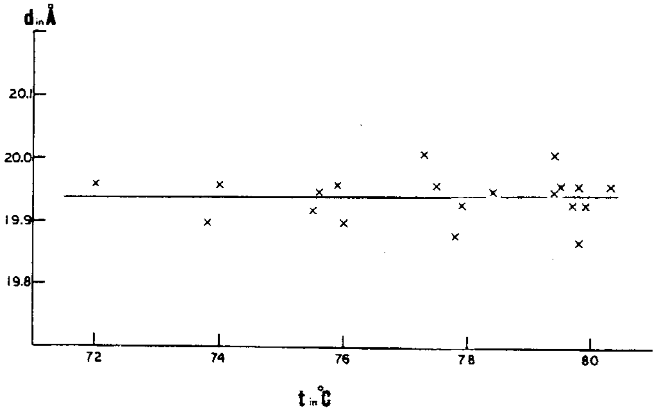

Figure 2. The layer thickness in the smectic phase as a function of temperature.

the measurements again is very good. The least-squares line has a slight positive slope (0.0007 Å/degree), not significantly different from zero ($\sigma = 0.004$). For the individual data points we found $\sigma = 0.04$ Å (which corresponds to an error in the measurement of the ring diameter of 0.04 mm).

THE NEMATIC PHASE

On the photographs of the nematic phase we measured the outer diffraction ring (associated with the intermolecular distance), and an inner diffraction ring (to be discussed in more detail further on in this paper) which was found in about the same position as the first order inner ring of the smectic phase.

The degree of alignment of the molecules varied, but was always much lower than in the smectic phase. Nematic phases at temperatures close to the N—L point, obtained by cooling the liquid phase, were always without visible alignment; if cooled down further to 0.2 or 0.3 °C above the S—N point, they nearly always showed moderate alignment. Nematic phases obtained by heating the smectic phase always showed moderate to weak alignment just above the S—N point, and gradually lost their alignment when the temperature was raised further. Remarkably, most alignment was shown by the nematic phase obtained from the smectic sample (mentioned above) which showed the least alignment (this was with a 1.0 mm capillary, the only one of this size used). But even here the ratio between the intensities of the maxima and the minima in the outer ring was only about 2.† The direction of preferred orientation made an angle of about 55° with the capillary axis in this case; the angles found in the other cases varied roughly from 50° to 90° (Demus and Sackmann(2) report that samples between flat glass plates were mostly pseudoisotropic).

All films were measured in four directions making angles of 0°, 45°, 90°, and 135°, respectively, with the direction of the maxima. There were no clear indications that the diameter of the outer ring was a function of the scanning direction, although the data from the photographs from the 1.0 mm capillary suggested that the diameter in the direction of the minima might be slightly smaller (about 0.5%) than in the direction of the maxima. The intermolecular distances D calculated from the average diameter for each photograph are

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† In all these cases no magnetic field was applied. In a case in which we applied a magnetic field, at an angle of about 60° to the axis of a capillary of 0.5 mm diameter, there was a fairly strong alignment of the molecules parallel to the field. When the magnet was removed, the alignment remained fairly strong ($I_{max}/I_{min} = 6$), but the direction of preferred orientation changed to an angle of about 80° with the capillary axis. The smectic phase obtained by cooling the nematic phase under the influence of the magnetic field showed again the alignment of the molecules parallel to the capillary, which appears to be typical for the smectic phase of EEB.

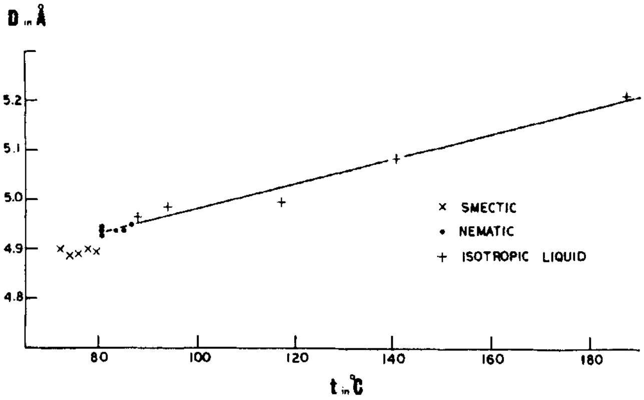

Figure 3. The intermolecular distance in the smectic, nematic, and isotropic phase as a function of temperature. For the smectic phase the data have been averaged in groups to reduce the number of points.

plotted in Fig. 3. The least-squares line through these values had a slope of 0.0017 Å/degree ($\sigma = 0.0010$), but this line is not shown on the graph, as will be discussed further in the section on the isotropic liquid phase. For the individual data points we found $\sigma = 0.01$ Å.

For the inner diffraction ring the difference in intensity between the maxima and the minima was usually much greater than for the outer ring. The most reliable measurements were those obtained from scans through the centers of the maxima, from photographs on which these maxima were well developed; only these data are reported on in this paper. The spacings, calculated from these measurements with the formula $2d \sin\theta = \lambda$, are presented in Fig. 4. The fact that we used d values calculated with the Bragg equation does not mean that we assume any kind of space lattice in this nematic phase. This equation was employed here only to be able to make some comparisons between the data obtained from the smectic, nematic, and isotropic phases (see under " Discussion ").

THE ISOTROPIC LIQUID PHASE

Here there are no problems due to alignment of the molecules in the sample, and the inner and outer rings were measured in several directions.

The outer rings were somewhat less intense than those from the

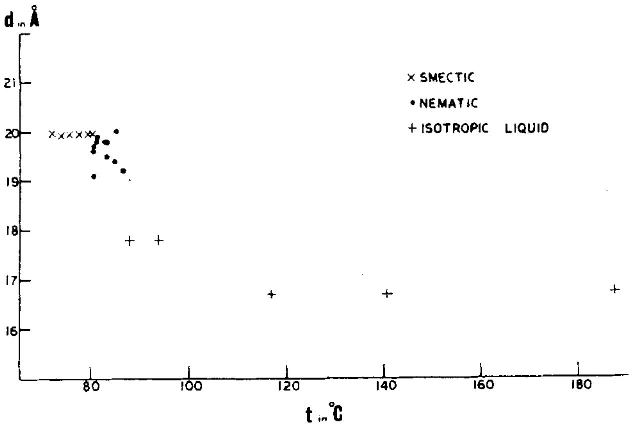

Figure 4. The lattice spacing calculated from the diameter of the inner ring as a function of temperature. For the smectic phase the data have been averaged in groups to reduce the number of points.

nematic phase, but they could still be measured well; the intermolecular distances calculated from these measurements are presented in Fig. 3. The slope of the least-squares line through these points was 0.0025 Å/degree (σ = 0.0003); for the individual data points σ was 0.02 Å. Comparing this slope with that found for the nematic phase we see that they are equal well within the limits of error. In addition, it was found that the least-squares line for the isotropic phase, if extrapolated into the nematic phase, passed very close to the center of gravity of the nematic data points, again well within the limits of error (the corresponding D values were: for the nematic data 4.940 Å with σ = 0.003, for the extrapolated line 4.944 Å with σ = 0.016). We decided, therefore, to calculate the least-squares line for the combined data from the nematic and isotropic phases, and to plot this line in Fig. 3. The slope of this line was 0.00250 Å/degree, σ = 0.00013.

The measurements of the diameter of the inner ring were rather inaccurate because this ring is not very pronounced in the isotropic phase. The d values obtained from these measurements (using Bragg's equation) are plotted in Fig. 4. No attempt has been made to draw a curve through these points, because the relatively large errors allow several different interpretations.

4. Discussion

The Inner Diffraction Ring from the Nematic and Isotropic Phases

A diffuse inner diffraction ring, at a diffraction angle of the order of 4°, has been observed by us for all nematic and cholesteric phases that we have studied so far, and also for the liquid phase of all liquid crystalline materials we have studied so far.(6) Literature data on this kind of diffraction effect are extremely scarce. Usually this ring apparently is intercepted by the beam stop or masked by the high background around the beam stop.

It should be emphasized here that one should distinguish between at least two different types of diffuse inner diffraction rings. First, there are the fairly weak rings as found in the nematic and isotropic phases of EEB, in all liquid and cholesteric phases we investigated, and in most of the nematic phases. Second, there are the quite intense rings found in the nematic phases of certain specific compounds(1,4); these rings have been interpreted by us(1) as indicating that a large number of molecules is organized in groups (called cybotactic groups) which have a much higher degree of order than the normal nematic phase (called the classical nematic phase). Starting from this theory, it would be possible to explain the much weaker inner rings as indicative of remnants of cybotactic groups. Although this interpretation may be correct for certain phases, we would like to propose here a much more general explanation for these weak inner rings, which does not require the organization of molecules in any kind of groups and which we feel is a much more probable explanation for most cases.†

Let us direct our attention to a single molecule of EEB in the nematic or the isotropic phase, and in particular to its electron density distribution projected onto the long axis of the molecule. In a first approximation this electron density may be considered

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† This explanation is not meant for, nor is it applicable to, the cybotactic nematic phases(1,5); it is intended only for the classical nematic phase (in which the only order is the approximate parallelism of each molecule with respect to its neighbors), for the isotropic phase, and for the cholesteric phase.

constant† except at the ends of the molecule, where it becomes much lower because at the ends we have only hydrogen atoms and possibly also some open space before we get to the next molecule. An electron density distribution like this, with an extended, more or less flat maximum in the middle and a minimum at each end, will give the same diffraction pattern as an electron density distribution with an extended minimum in the middle and a maximum at each end, or, in other words, as a diatomic molecule. The length of this " diatomic molecule " is equal to the distance between the electron density minima at the ends of the real molecule, and this distance may be taken as the " length " of the real molecule (this length will include half of the total free space, if any, at the two ends of the molecule).

The diffraction pattern from the hypothetical diatomic molecule will only show distinguishable maxima when its length is more or less constant. One will be able to observe it, therefore, only for fairly rigid molecules. Also, the length of the molecule should be significantly different from its width; otherwise, the diffraction pattern associated with the " diatomic molecule " will merge with the rest of the diffraction pattern (in terms of the two diffraction rings discussed in this paper: the inner and outer ring will come together). But if both conditions are fulfilled, the diffraction pattern associated with the " diatomic molecule " should be observable, and diatomic molecules of the proper length (of the order of 30 Å) would indeed give their main diffraction maximum in the region where we have observed the inner ring. We propose, therefore, that this diffraction effect is responsible for many of the weak inner diffraction rings we have observed (e.g., those in the nematic and liquid phases of EEB), and that similar diffraction effects(7,8) should occur for all non-crystalline materials containing molecules with sufficiently anisotropic shape and for which the long dimension is fairly constant.‡

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† It there are sufficiently well defined maxima and/or minima in the electron density distribution within the molecule, this may give rise to additional diffraction maxima. These are not discussed here.

‡ Other authors(9) have substituted heavy atoms at the ends of elongated molecules to be able to measure the length of the molecule. From the above discussion it follows that another way of using heavy atoms would be to substitute them in the center of the molecule; they will then enhance the already present diffraction effect from the electron density minima at the ends of the molecule.

Assuming, as we shall do in this paper, that the above theory is correct, the next question is what the relationship is between the length of the molecule and the position of the maxima of the inner diffraction ring. The answer to this question is that the relationship depends greatly upon the degree and the direction of alignment of the molecules in the sample. If the orientation of the molecules is completely random, the relationship between the molecular length l and the diffraction angle 2θ is given by the Keesom formula(1,10): $2l \sin\theta = 1.229\lambda$. If all the molecules are strictly parallel to each other and perpendicular to the direction of the incident beam, the relationship is $l \sin 2\theta = \lambda$. If all the molecules are strictly parallel to the direction of the incident beam, the relationship is $l\,(1 - \cos 2\theta) = \lambda$. It will be clear that one can calculate the length of the molecule from the position of the maxima of the inner diffraction ring only if the degree and the direction of alignment are known.

This variation in the relationship between l and θ is apparently what caused the large spread in our θ measurements from the inner ring in the nematic phase (Fig. 4), for this spread is much larger than expected from the error in measurements. Consequently, we have not been able to calculate any molecular length values for the nematic phase. This result is not entirely negative, however. The large spread in θ values shows that in the nematic phase of EEB the position of the maxima of the inner ring indeed depends upon the alignment, and this in turn indicates(5) that the nematic phase of EEB is not a cybotactic nematic phase but a classical nematic phase. Thus, the impossibility of determining l serves as an indication of the type of the nematic phase.

In the isotropic liquid we may assume a random arrangement of the molecules and use $2l \sin\theta = 1.229\lambda$. The values of l calculated this way are plotted in Fig. 5. As pointed out in the section on " The Isotropic Liquid Phase ", several different curves could be drawn through these points. In Fig. 5 we have drawn a straight, horizontal line† at an average l value (in the calculation of this value more weight was given to the more accurate measurements at lower

† Based on a comparison of the temperature dependence of measured densities with that of intermolecular distances obtained from X-ray photographs, Falgueirettes(11) concludes that the molecular length in *p*-azoxyanisole stays essentially constant in the liquid phase, and also when going into the nematic phase.

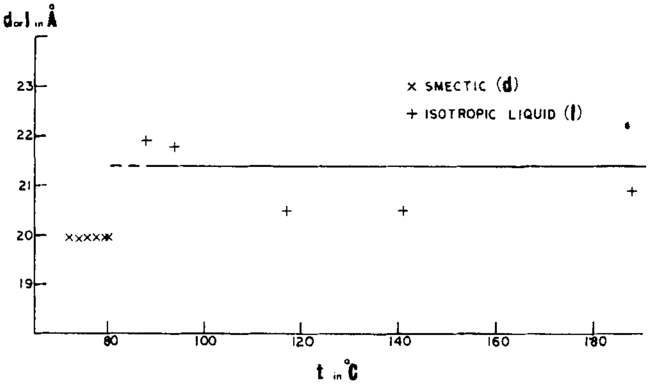

Figure 5. The layer thickness in the smectic phase and the molecular length in the isotropic phase, as a function of temperature. For the smectic phase the data have been averaged in groups to reduce the number of points.

temperature); the line was extended into the nematic phase as a broken line, to indicate that most probably the molecular length in the nematic phase is equal to that in the liquid phase.† This line falls at 21.4 Å, which is in very good agreement with the calculated molecular length of 21.6 Å which was obtained as follows. Assuming a planar molecule, a zig-zag arrangement for the end groups, and taking the directions of the end groups as close as possible to the direction of the line through the centers of the two benzene rings, and using the bond lengths and angles given in Table 2, the positions of the atoms were plotted on a piece of graph paper. The distance between the two hydrogen atoms at the ends of the molecule was measured and to this was added twice the van der Waals radius of hydrogen (1.17 Å). The distance so obtained (21.6 Å) was checked

Table 2 Bond Lengths and Angles Used in Model

C—C	1.52 Å	C⋯C	(benzene ring)	1.40 Å
C—O	1.42 Å	C—O	(in ═C—O—)	1.39 Å
C—H	1.08 Å	C—C	(in ═C—ϕ)	1.45 Å
C═N	1.32 Å	C—N	(in ═N—ϕ)	1.42 Å
C═O	1.23 Å			

All bond angles from a C or N atom carrying a double bond were taken to be 120°; all other angles between single bonds 112°.

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† See footnote on previous page.

by building molecular models (CPK models, from the Ealing Corporation); these models gave a distance of 21.3 Å, assuming the same van der Waals radius for hydrogen†.

As mentioned above, no nematic data are given in Fig. 5, but it may be noted here that all d values (Fig. 4) were smaller than 21.4 Å, or, in other words, that all measured 2θ values were larger than the one calculated from $2d \sin \theta = \lambda$, with $d = 21.4$ Å. Assuming that in the nematic phase $l = 21.4$ Å, the measured 2θ values are thus in agreement with the theory developed above, from which it follows that the observed 2θ value can never be smaller than the one obtained from the relation $l \sin 2\theta = \lambda$ (which is practically equal to $2l \sin \theta = \lambda$ for l values of 20 Å or more).

Summarizing this section on the inner ring data we would like to point out that use of the Bragg equation for these data would have left us with a number of strange results (Fig. 4): Most d values for the nematic phase are smaller than those for the smectic phase, and the d values for the isotropic phase are again smaller than those for the nematic phase; this is the opposite of the expansion one would normally expect upon heating. Also, the data for the nematic phase show a spread much greater than expected from the experimental errors. The theory for the inner diffraction ring, developed in this section, gives a satisfactory solution for these problems: The factor 1.229 leads to a good agreement between measured and calculated molecular length (also for other compounds$^{(12)}$) and to a good relation between the smectic and the isotropic data (Fig. 5); the varying relationship between l and θ explains the spread in the nematic data.

The Thickness of the Smectic Layers

The average value for the thickness of the smectic layers, over the temperature range investigated, is 19.941 Å, 1.46 Å (7%) less than the molecular length measured in the isotropic phase. Sackmann *et al.*$^{(13)}$ point out that they find this apparently too short layer thickness for all smectic A phases investigated by them, and we can confirm this on the basis of our own investigations on this and other compounds. Sackmann *et al.* suggest a non-stretched arrangement

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† Demus and Sackmann$^{(2)}$ report a length of 22.5 Å obtained from a Stuart-Briegleb model; we do not understand the large difference between their measurements and ours.

of the hydrocarbon chains as the cause for this effect. But in view of that facts that in crystalline solids the hydrocarbon chains are usually stretched and that our measurements on the isotropic phase indicate that the molecule is stretched in that phase too, this explanation does not seem to be very likely to us. Also, we found in another compound with much longer hydrocarbon chains that, although these chains were apparently unstretched at higher temperatures in the isotropic phase, they appeared to become more and more stretched as the temperature was lowered, approaching the fully stretched configuration at the S—L point.(12) It would seem unlikely that the chains would become unstretched again upon further cooling (i.e., in the smectic phase). Another explanation of the short distance between the layers would be that the molecules make a certain angle with the normal to the smectic planes; for EEB this angle would have to be about 21°. Sackmann *et al.* point out, however, that this would disagree with the microscopic observation that the aligned smectic A phase is optically uniaxial. Also, this skewed configuration would be in contradiction with our X-ray photographs of the aligned smectic phase of EEB, which show clearly that the direction of the long molecular axes (obtained from the position of the maxima in the outer ring(1)) is within a few degrees from the direction of the normal to the smectic planes (obtained from the position of the maxima in the inner ring). As a possible solution we should like to suggest here that the ends of the molecules of each layer penetrate the adjacent layers to a limited depth, in this case about 1.5 Å. Further investigations will be necessary, however, to obtain more conclusive evidence on this point. For instance, viscosity studies might be of interest, for the deeper the penetration, the higher the viscosity would be expected to be.

INTERMOLECULAR DISTANCES

The average intermolecular distance for the smectic phase is 4.894 Å (Table 3). It is of interest to compare this value with some dimensions from a model of the molecule. The thickness of a benzene ring is twice the van der Waals radius for carbon, 3.6 Å, and the width of a benzene ring (drawn with one carbon atom at the top and one at the bottom) is 6.7 Å, so the average of the two is 5.15 Å, 0.25 Å larger than the average intermolecular distance. This means

TABLE 3 Intermolecular Distances

Phase	Temperature	Distance†
Smectic	71.5 °C	4.890 Å
	80.4	4.898
Nematic	80.4	4.932
	87.0	4.950
Isotropic	180.0	5.182

† From the least-squares lines in Figs. 1 and 3.

that the packing of the molecules within the layers, although irregular (as indicated by the diffuse character of the outer ring). must be quite tight. A more or less free rotation of the molecules around their long axes is highly unlikely (this conclusion is in agreement with the position taken by Gray(14)). A herringbone packing, similar to that proposed by Gulrich and Brown,(15) would seem to be a much more probable model.

In the nematic phase the packing is not much looser (Table 3) and rotation of the molecules must still be regarded as very unlikely (again in agreement with Gray(14)). The interpretation of the small change in the measured intermolecular distance at the S—N point is not yet clear. This change in D may be a direct consequence of the change in phase, or, in view of the possibility of a variation of the intermolecular distance with the degree of alignment (see introductory paragraphs of Sec. 3), it may be caused by the large change in the degree of alignment at the S—N point.

At the N—L point there does not seem to be any change in the intermolecular distance, which suggests that the arrangement of the molecules with respect to each other is quite similar in the two phases† (this similarity is also indicated by the fact that the amount of heat associated with the N—L transition is very small; see Fig. 6): in the isotropic phase, too, the molecules are approximately parallel to their nearest neighbors, and, especially at temperatures close to the N—L point, there is little space for rotation of the molecules around their long axes.

It is tempting to suggest, on the basis of our observations, the following picture of the change in the molecular arrangement when

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† The same conclusion was reached by Falgueirettes(11) with regard to the isotropic and nematic phases of p-azoxyanisole.

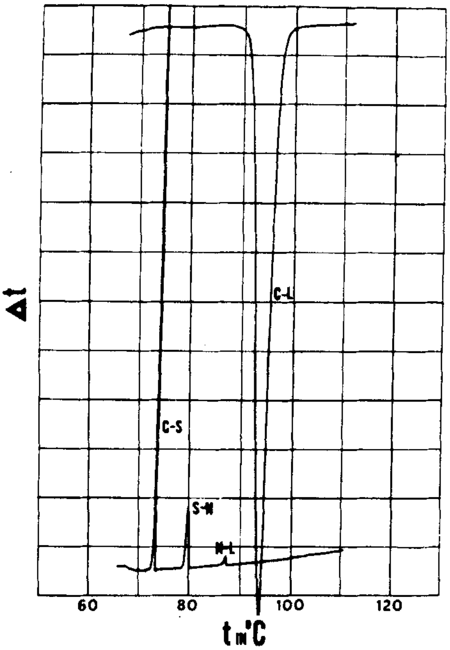

Figure 6. Differential thermal analysis plot from a sample of zone-refined EEB.

going from the smectic, via the nematic, to the isotropic phase of EEB. In all three phases (at least for temperatures not too far above the N—L point) the arrangement of the molecular planes of neighboring molecules is essentially the same (e.g., a herringbone-type packing), and the main change upon going from one phase to another takes place in the longitudinal arrangement of the molecules: in the smectic phase the relationship between the positions of neighboring molecules is fixed and regular, in the nematic phase this relationship is quite irregular but still more or less fixed,† and in the isotropic phase the molecules are free to move in the direction of the long axis.

VOLUME EXPANSION COEFFICIENTS AND DENSITIES

Assuming an idealized arrangement of the molecules, each molecule occupying (in the direction of its long axis) a space of length l

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† This kind of arrangement for the nematic state was suggested to us by Dr. D. P. Shoemaker and by Dr. R. K. Mishra.

(or d, in the smectic phase) and surrounded (in the plane perpendicular to its long axis) by six other molecules at a distance D, it is possible to calculate the volume expansion coefficient and the density. A comparison of these calculated values with experimentally determined ones constitutes a further test of the correctness of the theory and the formulas used in this paper to obtain D, l, and d.

With a molecular arrangement as described in the above paragraph, the volume per molecule is $v = lD^2 \cos 30°$ (replace l by d for the smectic phase). From the values of d, l, and D at different temperatures we have calculated the volume expansion coefficient as $\beta = (v_2/v_1 - 1)/(t_2 - t_1)$. These values of β are presented in Table 4 together with values obtained from the literature. The value for β in the isotropic phase of EEB compares very well with those of the isotropic and nematic phases of the two other liquid crystalline materials (MBC and PAA), and all these are comparable to the value for phenol (though the latter is somewhat larger). The value of β for the smectic phase of EEB is much smaller, and tends more towards that of solid materials like paraffin, but the accuracy of this β value is much less than of β for the isotropic liquid, so no conclusions can be drawn at this point.

TABLE 4 Volume Expansion Coefficients in 10^{-5} (°C)$^{-1}$

Compound		Isotropic	Nematic	Smectic	Solid
Ethyl-*p*-ethoxybenzal-*p*-aminobenzoate	(EEB)	83	—	40	—
p-Methoxybenzylidene-*p*′-cyanoaniline[15]	(MBC)	92	97	—	—
p-Azoxyanisole[16]	(PAA)	75	72	—	—
Phenol[17]		109	—	—	—
Paraffin,[17] 0–16 °C		—	—	—	32
Caoutchouc[17]		—	—	—	23

From the molecular weight (297.35) and the volume per molecule we calculated also the densities at various temperatures. These are given in Table 5, again compared with literature data on other compounds. We see that the density of the isotropic phase of EEB compares very well with those of the isotropic and nematic phases

TABLE 5 Densities in gr/cm^3

Compound†	Isotropic	Nematic	Smectic	Solid
EEB	1.09 (87.6°)‡	1.09 (80.4°)§	1.196 (71.4°)	—
	1.01 (180°)	—	1.192 (80.4°)	—
MBC[15,18]	1.076 (120°)	1.093 (107°)	—	1.22
PAA[16,19]	1.138 (142°)	1.182 (100°)	—	1.38
EAP[18]	—	—	—	1.21

† EAP is *p*-ethoxybenzol-*p*-azophenyl propionate; for the other abbreviations, see Table 4.

‡ The values in parentheses are the temperatures in °C at which the densities were determined.

§ Assuming the same molecular length as in the isotropic phase (21.4 Å).

of MBC.† The densities of the solid phases of MBC and EAP (both compounds that give liquid crystalline phases on melting) are very similar to each other, and the density of the smectic phase‡ of EEB is very close to the densities of these solid phases; this is in agreement with what one would expect, since the packing of the molecules in a smectic phase is most probably very similar to that in the solid phase.

5. Summary

We have presented in this paper accurately measured molecular parameters for the smectic, nematic, and isotropic phases of EEB. On the basis of these data and other observations we have drawn some general conclusions with regard to the packing of the molecules in these phases. There appears to be no room for a more or less

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† The densities of all phases of PAA (especially the solid and the nematic phases) appear to be higher than the corresponding densities for the other compounds listed in Table 5. It is of interest to note here that the nematic phase of PAA appears to contain cybotactic groups of molecules (higher homologues of PAA show strong evidence of the presence of cybotactic groups, as may be seen from a comparison of references 1 and 4). We suggest that the high density of the nematic phase of PAA is related to the existence of cybotactic groups, since these groups have a more regular arrangement of the molecules as compared with a classical nematic phase, and thus probably will give rise to a higher density.

‡ This density is calculated assuming that the molecules stand perpendicular to the smectic planes (arguments in support of this have been given in the section on " The Thickness of the Smectic Layers ").

free rotation of the molecules around their long axes, not even in the isotropic liquid. In the isotropic liquid the experimentally determined molecular length (21.4 Å) is very close to the calculated length of the stretched molecule (21.6 Å), but the thickness of the smectic layers (19.941 Å) is significantly less than this. The angle between the long molecular axes and the smectic planes is found to be very close to 90°, in agreement with the contention of Sackmann *et al.* that in the smectic A phase the molecules stand perpendicular to the planes. The nematic phase appears to be a classical nematic phase, *i.e.*, there is no significant ordering of the molecules apart from the near parallelism of the long axes of neighboring molecules.

Several of these conclusions depend upon the correctness of the formulas we used in the calculation of the molecular parameters, and of the theories behind the formulas. To test these formulas we calculated densities and volume expansion coefficients on the basis of the X-ray data, and we have shown that these calculated densities and expansion coefficients agree remarkably well with experimentally determined values for other liquid crystalline compounds. This agreement may be considered as supporting evidence indicating that the theories and assumptions used in the calculations are correct. It seems appropriate to summarize here these theories and assumptions.

(1) The intermolecular distance D between elongated molecules in the smectic, nematic, and istropic phases is obtained from the diffraction angle of the outer diffraction ring with the formula $2D \sin\theta = 1.117\lambda$.

(2) The effective length l of an elongated molecule in the istropic phase (and in the randomly oriented classical nematic phase) is obtained from the diffraction angle of the inner diffraction ring with the formula $2l \sin\theta = 1.229\lambda$.

(3) For the calculation of the densities of the smectic, nematic, and isotropic phases of EEB one can assume an idealized arrangement of the molecules, in which each molecule is occupying a space of length l (or d, in the smectic phase) and is surrounded by six molecules at a distance D.

Acknowledgements

The author gratefully acknowledges the help of several members of the staff of the Liquid Crystal Institute: Dr. P. R. Patel and Mr. A. Mehta, who prepared the compound and performed microscopic and DTA studies; Dr. J. T. S. Andrews, who zone-refined the material; Mr. P. Standley, who assisted in collecting the data; and Mr. Y. S. Lee, who made the DTA graph reproduced in Fig. 6. He also thanks Mr. W. Y. Lee for permission to use his density data prior to publication.

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