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X-ray Diffraction Studies of (—)-2-Methylbutyl p-(N-(P-Methoxy Benzylidene) Amino) cinnamate

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In this paper we have reported the X-ray diffraction studies of (−)-2-methyl butyl *p*-(N-(P-methoxy benzylidene) amino) cinnamate at different temperatures. On the basis of X-ray diffraction and texture study the substance is found to have the crystallisation path (phase transition) as given below

$$\text{solid} \underset{\sim 16^{\circ}\text{C}}{\overset{53^{\circ}\text{C}}{\rightleftharpoons}} \text{smectic B} \overset{59^{\circ}\text{C}}{\rightleftharpoons} \text{smectic A} \overset{78^{\circ}\text{C}}{\rightleftharpoons} \text{cholesteric} \overset{97^{\circ}\text{C}}{\rightleftharpoons} \text{isotropic}$$

X-ray diffraction patterns were recorded on a Laue camera with high-temperature attachment. The temperatures were measured and regulated (within ±0.5°C) with a thermocouple inserted in the block. Textures at different temperatures were observed under polarising microscope with hot base. Apparent molecular length, thickness of the layers and average distance between the molecules at different temperatures have been calculated. From X-ray diffraction pattern and also from microscopy smectic A and smectic B phases have been identified.

1 INTRODUCTION

X-ray diffraction studies of (−)-2-methyl butyl *p*-(N-(*p*-methoxy benzylidene)-amino) cinnamate (MBAC in short) at different temperatures are reported in this paper. This is a part of our programme for the evaluation of structures of various mesophases and determination of order parameters of aligned samples. Liao *et al.*[1] have studied Brillouin scattering for this sample. They have attributed a smectic A and smectic B modification to the substance. Steady-flow viscosity data have been given for this by Friedman *et al.*[2] Gray[3] have given the transition temperatures of (−)-2-methyl

butyl *p*-(N-(P-methoxy benzylidene)-amino) cinnamate along with the transition temperatures of other *n*-alkoxy group. The transition temperatures from solid to smectic, smectic to cholesteric and cholesteric to isotropic as given by them are 53°C, 78°C and 98°C respectively. Leclercq *et al*[4] have also studied the phase transitions of this compound. The existence of two smectic phases has also been observed by them. Till now no X-ray diffraction data have been published for this substance. We have identified the various mesomorphic phases of MBAC by microscopic, calorimetric and X-ray diffraction studies. The structure of the substance is shown in the Figure 1.

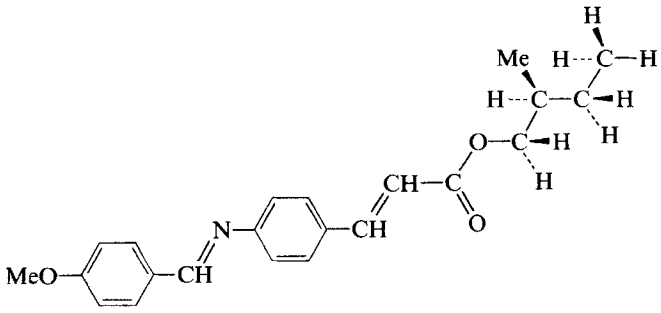

FIGURE 1

According to the literature the sample MBAC has the following mesomorphic range.

$$\text{Solid} \xrightarrow{53^\circ C} \text{smectic} \xrightarrow{78^\circ C} \text{cholesteric} \xrightarrow{97^\circ C} \text{isotropic}$$

On the basis of our X-ray and microscopic studies it is found to have the following crystallization path.

$$\text{solid} \underset{\sim 16\,^\circ C}{\overset{53^\circ C}{\rightleftharpoons}} \text{SmII} \overset{59^\circ C}{\rightleftharpoons} \text{Sm I} \overset{78^\circ C}{\rightleftharpoons} \text{cholesteric} \overset{97^\circ C}{\rightleftharpoons} \text{isotropic}$$

2 EXPERIMENTAL METHODS

The compound MBAC obtained from Eastman Kodak Company was dried in vacuum desciccator for two hours. X-ray diffraction photographs of MBAC were recorded on a Laue camera with a high-temperature attachment and modified collimating system (Figure 2a, 2b) using Ni-filtered CuK_α radiation. The temperatures were measured and regulated with the help of a thermocouple inserted in a brass block with the accuracy of ± 0.5°C. The sample in the powder form was contained in a glass capillary

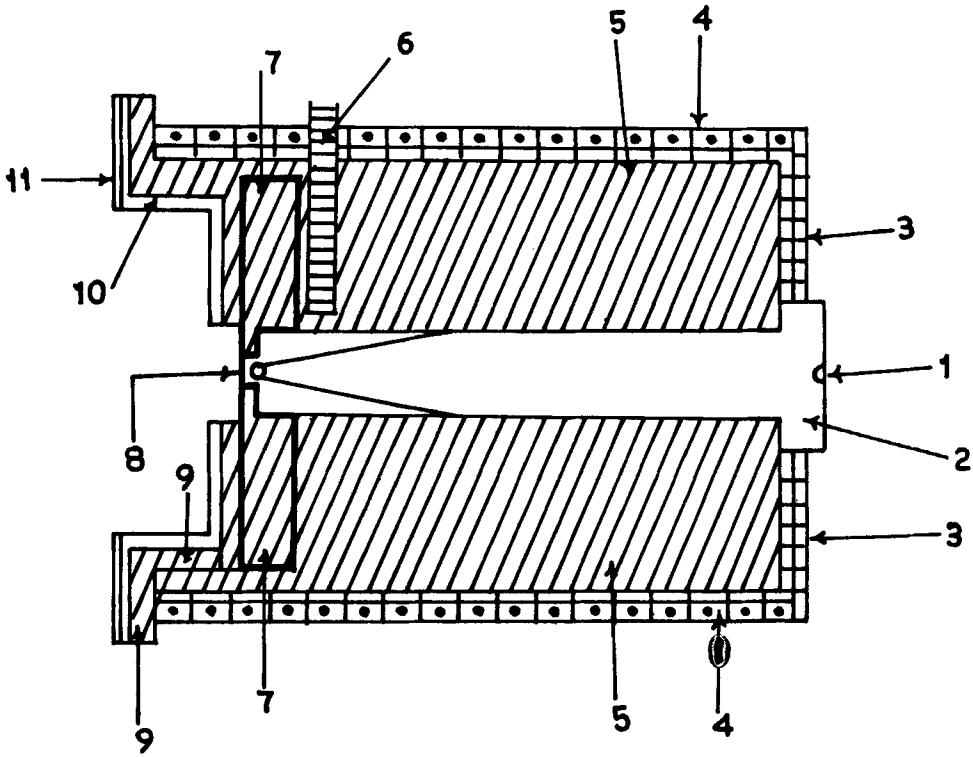

FIGURE 2(a) Sectional diagram of the sample holder: (1) Direction of X-ray; (2) Collimator; (3) Asbestos insulation; (4) Insulation and heater winding; (5) Cylindrical brass chamber; (6) Thermocouple; (7) Specimen container brass disc); (8) Specimen; (9) Brass cover for specimen container; (10) Lead; (11) Asbestos insulation.

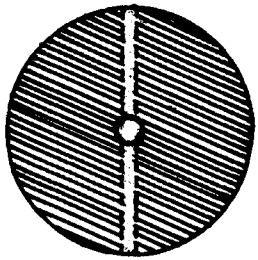

FIGURE 2(b) Capillary holder.

and a brass disc in contact with the brass block had a hole drilled along its diameter to hold the capillary. All the photographs were scanned with the help of an optical densitometer model No. DM 803 (Electronic Corporation of India Ltd.). Sample to film distance was measured accurately by calibrating with (111) reflection of aluminium.

3 EXPERIMENTAL RESULTS

The diffraction photographs of the sample were taken at different temperatures, starting from the solid phase at room temperature to isotropic phase. The melting point is found to be 53°C. Below 53°C we got powder patterns of polycrystalline sample. Photographs below 78°C showed that the sample was in the smectic phase and above 78°C cholesteric phase was observed. The compound changed to isotropic liquid at 97°C. X-ray photographs showed the existence of two smectic phases, smectic II and smectic I. Photographs of smectic II phase showed one sharp outer ring and one sharp inner ring (and its second-order one) characteristic of the smectic B phase. The smectic II phase is therefore a B phase, which was later confirmed by our microscopic observations. Photographs of smectic I phase showed one sharp inner ring and a diffuse outer ring. This phase may be smectic A or smectic C phase. The substance was then cooled down to room temperature, it was found to be very sticky. A diffraction photograph was taken at room temperature. The diffraction pattern was interesting. We no longer got a powder photograph but a pattern of one sharp inner ring and a sharp outer ring as shown in Figure 3. This phase is the same as the smectic II phase that is B phase. Another series of photographs of the sample in the same capillary was taken while heating as well as while cooling. We never got a powder photograph below 53°C, even at room temperature. The process was repeated with a fresh sample. In each and every case it was found that once the sample is heated above 53°C the solid phase could not be observed at room temperature again. If it is not heated we get photographs of polycrystalline sample. Confirmation of the fact that there was no change in chemical composition was performed by taking the infra-red spectra of the sample twice (first with the original sample at room temperature and then with the sample which was cooled down to room temperature after heating up to 53°C). DSC (differential scanning calorimetry) was done for the sample and phase changes were observed approximately at 98°C, 80°C and 59°C. Liao *et al.*[1] reported that below 47°C the substance is supercooled. As we do not have at present any arrangement for taking X-ray diffraction photographs below room temperature, the sample holder with the sample was

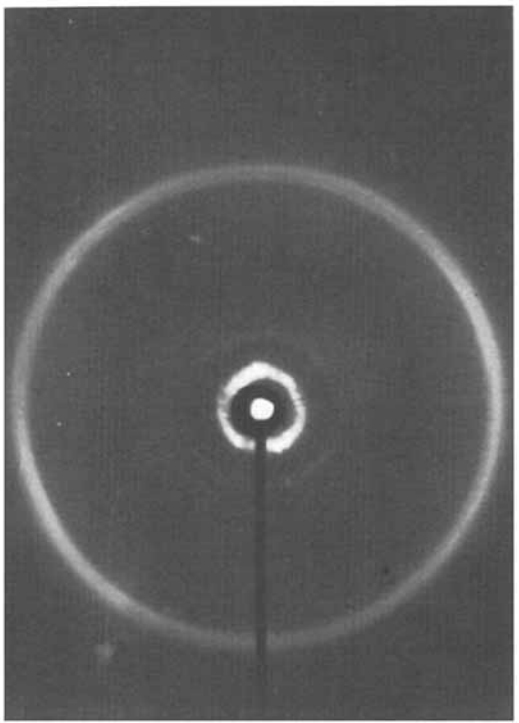

FIGURE 3 X-ray diffraction photograph of smectic B phase at room temperature (during cooling).

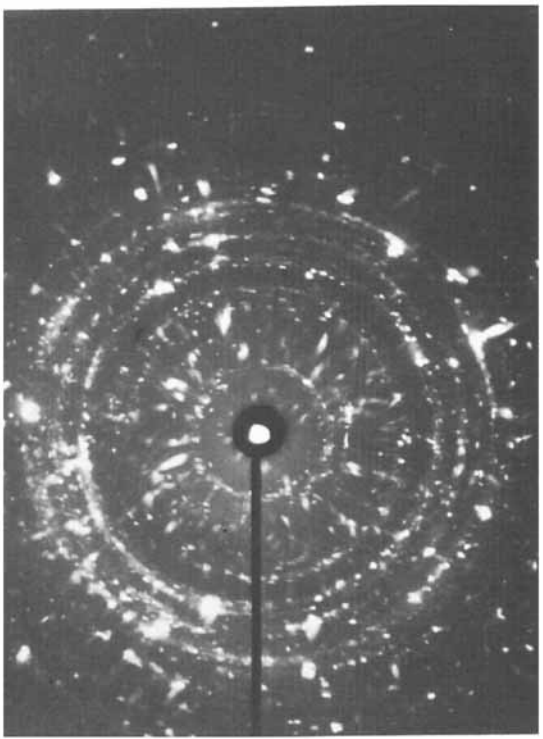

FIGURE 4 X-ray diffraction photograph of the solid phase at room temperature.

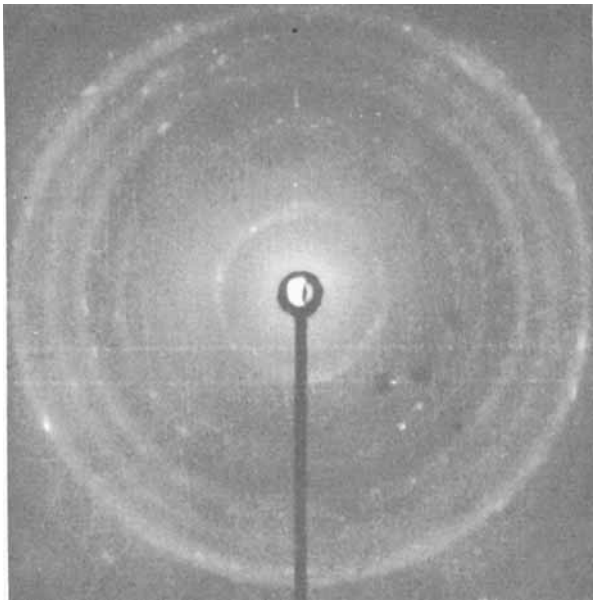

FIGURE 5 X-ray diffraction photograph at 45°C (during heating).

kept vertically in a thermoflask containing ice and the temperature was observed. At about 16°C there was a marked change in the appearance of the substance. The substance changed its phase at this temperature. An X-ray diffraction photograph was taken at room temperature (22°C) and we got a solid phase picture as shown in Figure 4. We repeated the whole process with fresh sample and took X-ray photographs while heating and also while cooling. Photographs at 45°C, 52°C, 55°C and 60°C taken while heating are shown in Figure 5, 6, 7, and 8 respectively.

Photographs of 55°C and 60°C taken while cooling are exactly the same as while heating. But patterns at 45°C and 52°C are just like the photographs shown in Figure 4, i.e., the photograph of smectic B phase.

Hot stage polarised microscopy

The melting behaviour was examined by using polarising microscope equipped with a hot stage which has been fabricated in our laboratory. The observations were performed under cross polarizers and magnification was 150X. The sample was placed between cover slips. The substance melted at 53°C. During heating we could not observe a phase change at

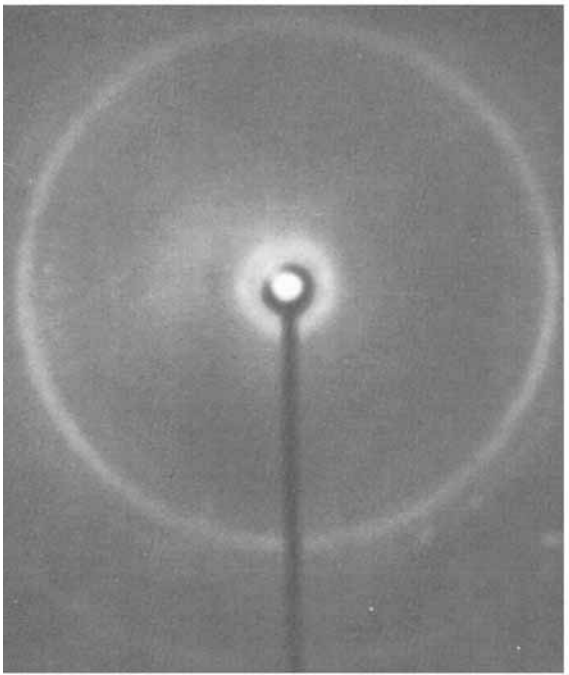

FIGURE 6 X-ray diffraction photograph at 52°C (during heating).

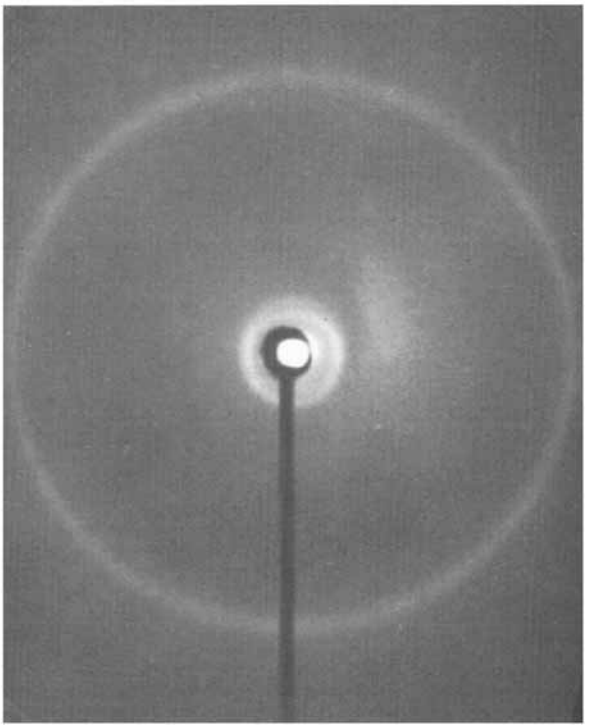

FIGURE 7 X-ray diffraction photograph at 55°C (during heating).

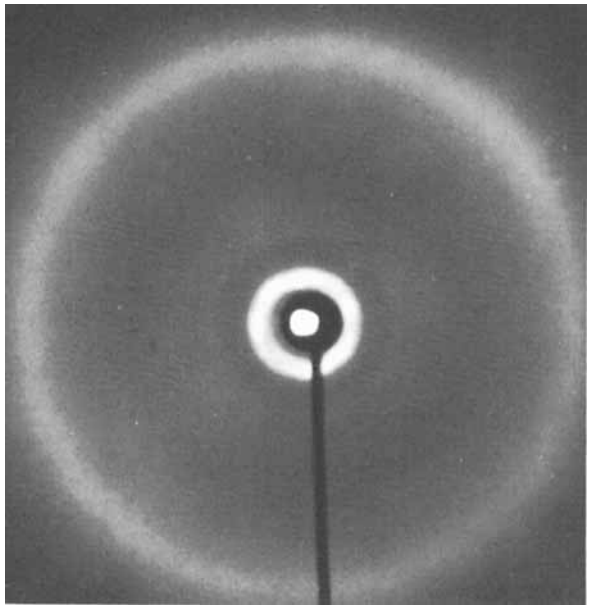

FIGURE 8 X-ray diffraction photograph at 60°C (during heating).

59°C on our first attempt. Above 59°C we got focal conic texture characteristic of smectic A[6] phase, below 59°C we could not identify the texture which looked somewhat like broken focal conic type. Our photographic studies however showed the existence of smectic B phase in the temperature range 53°C–59°C. Our microscopic observation missed the B phase while heating. We started with fresh sample. A phase change was observed at 59°C while heating, but the texture characteristic of smectic B phase could never be detected. At 78°C the change of colour with focal conic texture of cholesteric phase was observed. The isotropic phase was seen at 97°C. During cooling focal conic texture of cholesteric phase with several colours were observed. Below 78°C textures of smectic A, both the focal conic[6] and fan type[7] were observed very distinctly. We had not been successful with our conoscopic measurement, so we cannot say definitely whether the phase is uniaxial or biaxial, but from our texture studies we identify this phase to be smectic A. From 58°C to room temperature (22°C) the sample showed mosaic[8] and fan texture of smectic B phase. The sample in the cover slips was then kept in ice for a few hours and the texture observed was found to be that of solid phase. Heating and cooling runs did not yield identical results indicating that super cooling was present. A survey of the phase change from X-ray

photographic analysis and texture studies give the following results:

$$\text{Solid} \underset{\sim 16^\circ C}{\overset{53^\circ C}{\rightleftharpoons}} \text{smectic B} \overset{59^\circ C}{\rightleftharpoons} \text{smectic A} \overset{79^\circ C}{\rightleftharpoons} \text{cholesteric} \overset{97^\circ C}{\rightleftharpoons} \text{isotropic}$$

4 DISCUSSIONS

Thus microscopy and X-ray studies confirmed that the sample MBAC has a smectic B phase, smectic A phase and cholesteric phase. This result is in very good agreement with the observation of Liao *et al.*[1] In accordance with the observation of Friedman *et al*[2] a viscosity maximum is observed at the cholesteric isotropic transition (during microscopic study).

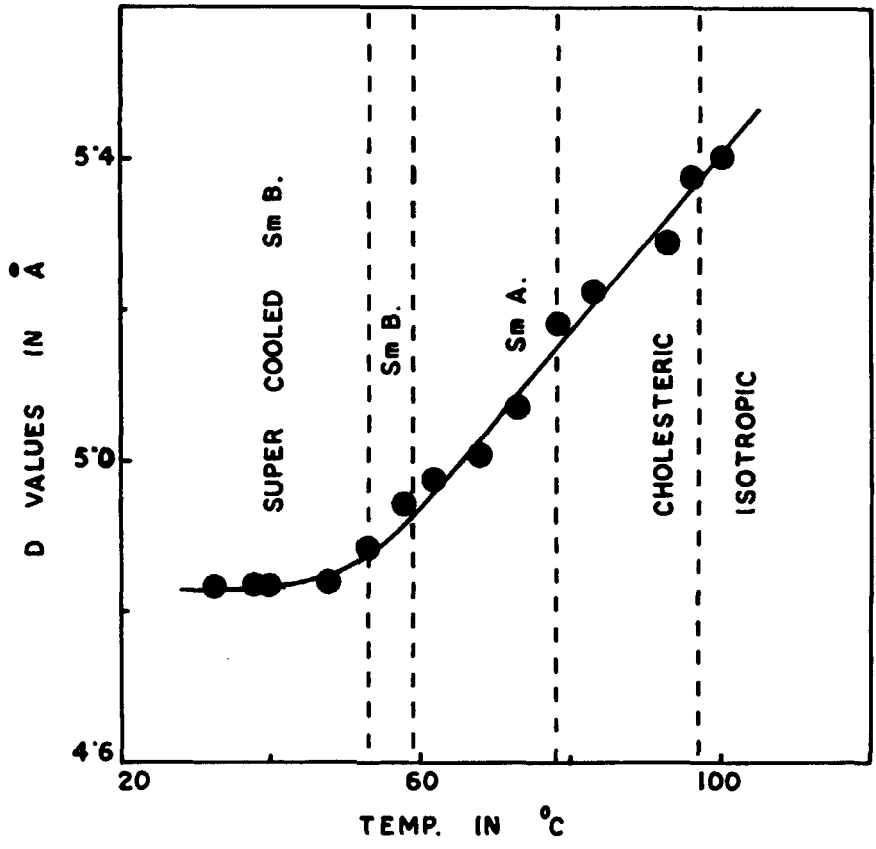

FIGURE 9 Variation of D with temperature.

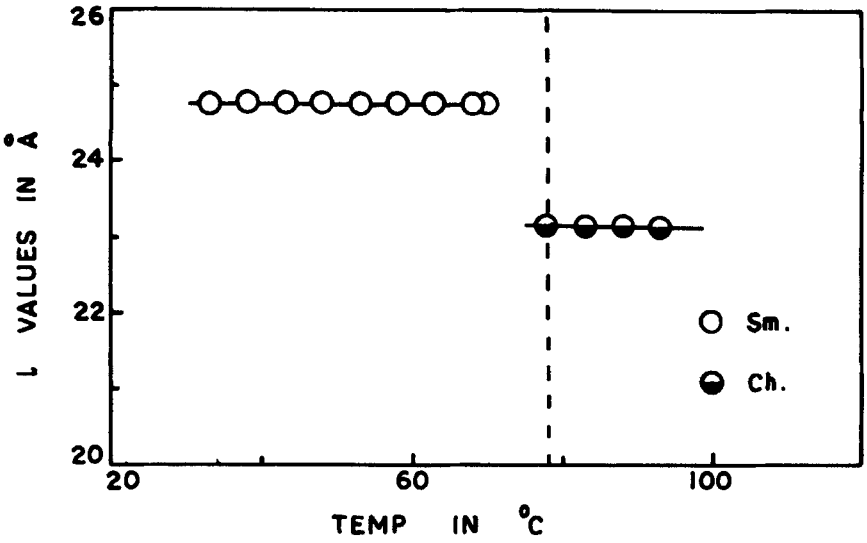

FIGURE 10 Variation of l with temperature.

Average distance between neighbouring molecules (D) and apparent molecular length or the thickness of the smectic layer l are calculated from X-ray diffraction photographs. D is calculated from the diameter of the outer ring with $2D \sin\theta = 1.117\lambda$ as given by de Vries,[9] l is calculated using Bragg's formula $2l \sin\theta = nx$ ($n = 1$ in the case of cholesteric and $n = 2$ in the case of smectic). Variation of D and l with temperatures are given in Figures 9 and 10. These are the values calculated from the photographs taken while cooling. Variation of D and l with temperature in different smectic phases has been discussed by de Vries.[10] In our case it is found that D increases with temperature except in the supercooled region, where it remains fairly constant. l values remain the same in the smectic region but there is a sharp decrease in the cholesteric region as shown in Figure 10. With the help of the Stereomodel Units (W. Bochi glass aparate fabrik 920 Flawil) we have constructed the possible structure of MBAC and measured the molecular length L in its completely extended form which is 23.14 Å. In the smectic range the molecular thickness l is found to be 24.78 Å which is little larger than L. Leadbetter *et al.*[11] in their study of the structure of smectic phases of some compounds found L to be much smaller than l. They explained it to be due to some form of bilayer structure. In our case difference of l and L is not so large and in our opinion this may be due to the staggered parallel orientations of the molecules in the layers. The staggering is due to the hindrance caused by branching of hydrocarbon chains.

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