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Sn-119 Mössbauer effect study of two Sn-bearing liquid crystalline materials

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A ^{119}Sn Mössbauer, lattice dynamic orientational study, at 77 K, of the smectic *B* glass phase of the Sn-bearing liquid crystals (LC) *p*-(11-trimethyltin)undecyloxy-benzilidene-*p*′-*n*- butylaniline (Sn-UBBA) and *p*-(11-trimethyltin)undecyloxy-benzilidene- *p*′-octylaniline) (Sn-UBOA), and solutions of these liquid crystals in LC of similar structure which do not contain Sn as part of their molecules, is presented. The Sn-bearing liquid crystals were designed and synthesized specifically for this study and their synthesis is described. The samples were aligned by cooling from the melt in the presence of a magnetic field. For the samples of Sn-UBBA and Sn-UBOA, the experimental linewidth appears to depend on the orientational angle θ. This is explained as due to the non-negligible sample thickness and the rff versus θ variation. These θ dependencies were used to extract the absolute fractions for various orientations of Sn-UBBA and then the corresponding Debye temperatures $\Theta_D(\theta)$. For the other samples the lattice contribution to the nuclear vibration anisotropy ϵ_L was found. A comparison of these parameters suggests that the alignment found in the solutions is similar to the pure LC. Further,the existence of a nematic phase is not important in the alignment of smectics via cooling from the melt in the presence of a magnetic field. The effect of the aligning field intensity on the quality of the alignment is discussed. The θ dependence of the apparent line position for pure Sn-UBBA and Sn-UBOA is explained as due to the presence of a weak unresolved doublet, probably induced by the anisotropic enviornment of the Sn nuclei in the LC.

INTRODUCTION

In this work we present the results of ^{119}Sn Mössbauer orientational studies of four smectic *B* liquid crystalline glasses, at 77 K. The four samples are (1) pure *p*-(11-trimethyltin)undecyloxy-benzylidene-*p*′-*n*-butylaniline (Sn-UBBA), (2) pure *p*-(11-trimethyltin)-undecyloxybenzylidene-*p*′-*n*-octylaniline (Sn-UBOA), (3) 8.05% Sn-UBBA in *p*-(12-12-dimethyl)tridecyloxybenzylidene-*p*′-*n*-pentylaniline (TBPA), and (4) 8.31% Sn-UBOA in *p*-(12-12-dimethyl) tridecyloxybenzylidene-*p*′-*n*-octylaniline (TBOA).

The liquid crystalline compounds used in this investigation were designed and synthesized with several initial objectives. Tin was to be incorporated in the primary (covalently bonded) structure of the compound whose mesophases were under study, thereby providing specific dimensional information for the molecules of the mesophase relative to the Mössbauer probe-nucleus. The molecular analogs with carbon replacing tin in these mesomorphic compounds were also prepared; these have methyl branching at the terminus of the benzylidene moiety in exact structural analogy to the trimethyltin function. These compounds provide a measure of the extent to which tin perturbs the mesophase properties of these materials and also provide the necessary link to the large class of mesomorphic anils for which extensive data already have been published and which have, for the most part, unbranched terminal chains.

The chemical formulas, the transition temperatures, the phases, and the transition enthalpies and entropies of Sn-UBBA, Sn-UBOA, TBPA, and TBOA are given in Fig. 1. The phases of all these liquid crystals (LC) have been identified microscopically, and their transition temperatures were confirmed by differential scanning calorimetry (DSC) studies, which also yielded the transition enthalpies and entropies of all four compounds.[1] The temperature of the glass-solid transition of Sn-UBOA was determined with the use of Mössbauer spectroscopy.[2,3]

It is important to note that in contrast to previous ^{57}Fe and ^{119}Sn Mössbauer studies of frozen liquid crystals, in which the Mössbauer nuclei were incorporated into the liquid crystalline matrix by the dissolution of an appropriate solute into the liquid crystal under study, in this work pure Sn-bearing liquid crystalline compounds were studied as well. The advantages of studying liquid crystalline compounds which include Mössbauer nuclei in their constituent molecules are obvious. In particular, the effects such as misalignment caused by solute molecules which differ in size and shape from the host molecules are avoided. Also, the introduction of localized modes caused by the probable local distortion of the liquid crystal matrix in the neighborhood of the solute molecules is avoided.

Because the Mössbauer spectra of our samples exhibited no measurable quadrupole splittings, we were unable to measure an order parameter for these glasses. However, we determined the mean-square vibrational amplitude of the ^{119}Sn nuclei and the intermolecular contribution to the nuclear vibrational anisotropy. The methods of determination of these parameters as well as a study of the variation of the apparent line position and the linewidth versus the orientation angle θ is presented in the following sections. Here θ is the angle between the molecular preferred direction (the director)

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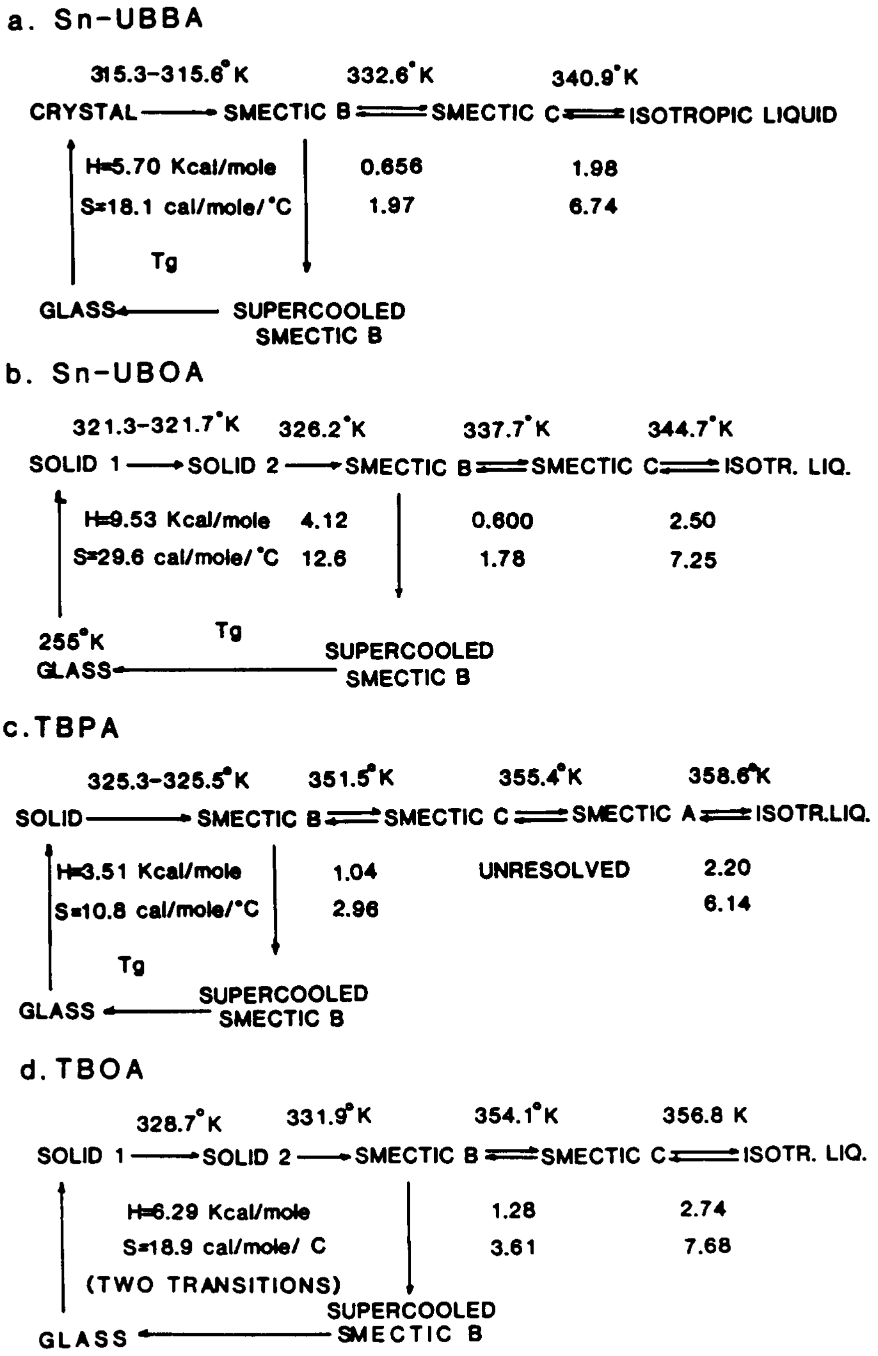

FIG. 1. Thermal data for (a) Sn-UBBA, (b) Sn–UBOA, (c) TBPA, and (d) TBOA.

of the liquid crystalline glass and the normal to the flat faces of the disc shaped sample (which coincides with the direction of the γ-ray beam during the Mossbauer experiment).

Materials syntheses

After studies of a number of organotin compounds, it was determined that compounds with only carbon bonded to tin would best meet our objectives. Although tin–carbon bonds are more reactive than carbon–carbon bonds because of their greater length, higher polarizability, and the ability of tin to expand its valence shell beyond eight electrons, they are sufficiently inert both to air and water to warrant their use in preparing potential mesomorphic compounds. The tin–carbon bond also offers the advantage of early placement in a synthetic sequence because of its stability to nucleophilic reagents. Thus reactions such as lithium aluminum hydride reductions, Grignard reactions, and alkaline hydrolysis can be used if the functional group to be altered is in the beta position or beyond with respect to the tin atom. Electrophiles such as halogens or strong aqueous acids should be avoided because of their ability to react with the tin–carbon bond. Saturated alkyl–tin compounds are more stable toward nucleophilic and electrophilic cleavage than are aryl–tin compounds.

EXPERIMENTAL METHODS

Transition temperatures for mesophases were established by measurements using a calibrated Mettler

FP-2 microscope hot stage modified for low-temperature measurements[4] and equipped with a Leitz Ortholux polarizing microscope. Heating and cooling rates of 2 °C/min were employed through all observable transitions. Spectra were obtained on Varian A-60 or EM-360 (pmr), Perkin–Elmer 337 (IR) or AEI MS-12 (ms) spectrometers. Thermal transitions and calorimetric data were obtained on a Perkin–Elmer DSC-1B differential scanning calorimeter. Gas chromatographic analyses were performed on a Hewlett Packard 7620A gas chromatograph equipped with FID and using a 6 ft. ×1/8 in. 10% UC-W9880-100 column. Reagents and solvents were obtained from major commerical supply houses and were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, or in house (tin) by the procedures of Poller,[5] Gilman, and Rosenberg.[6]

4-(11-Trimethyltin)undecyloxybenzylidene-4′-*n*-alkylanilines (Sn-UBBA and Sn-UBOA)

Trimethyltin hydride. Greaseless joints were used during reaction and workup procedures. Trimethyltin chloride (112.3 g, 0.565 mol) in 100 ml of dry diglyme was added to a suspension of lithium aluminum hydride (10.5 g, 0.28 mol) in 300 ml of dry diglyme heated to 100–125 °C over a 2 h period. During addition a vacuum (~200–250 Torr) was applied with a concurrent nitrogen flow and the trimethyltin hydride distilled as it was formed. Redistillation yielded pure trimethyltin hydride (56 g, 0.34 mol, 61%), bp 61 °C/atm pressure, bp 60 °C/760 Torr (Ref. 7). IR (cm^{-1}) neat, 1830 (Sn–H). The hydride was sealed in ampoules under nitrogen for future use.

11-*Trimethyltinundecan*-1-ol. 10-undecen-1-ol (29.6 g, 0.176 mol), trimethyltin hydride (27.6 g, 0.168 mol), and fresh azobisisobutyronitrile (1.62 g, 5 mol%) were added to a Lab Glass, Inc. (LG 9375) pressure reaction apparatus and sealed under nitrogen. The mixture was heated at 55 °C (~48 h) while monitoring the reaction by IR (disappearance of Sn-H stretch at 1815 cm^{-1}). The reaction mixture was cooled and a white crystalline precipitate of organotin polymers was filtered (5 g, mp >300° sublimation; % Sn found: 76.32%, 76.35%). Distillation of the filtrate gave fractions boiling over a range (124°–144°/0.15 Torr); IR monitoring indicated Sn–O reaction as well as addition to C=C. Combined fractions from two runs (16.2 g) were refluxed with malonic acid solution (1.46 g, 0.06 mol in 20 ml ether) for 15 min to cleave the Sn–O bond. Precipitated trimethyltin malonate (1.5 g mp 194° dec) was filtered and the crude product distilled to give pure 11-trimethyltinundecan-1-ol (12.4 g, 0.037 mol, 61.7% of unrecovered 10-undecen-1-ol) bp 122°/0.2 Torr IR (neat), 3310 (-OH); pmr (CDCl_3): $\delta 3.55$ (t, 2, $J=6$, $-\text{O}-\text{CH}_2-$); $\delta 2.00$ (s, 1, $-\text{OH}$); $\delta 1.84-0.7$ (m's, 20, $-[\text{CH}_2]_{10}-$); $\delta 0.06$ (s, d's, 9 $J\ {}^{119}\text{Sn}-\text{C}-\text{H}=52$, $J\ {}^{117}\text{Sn}-\text{C}-\text{H}=50$, $-\text{Sn}[\text{CH}_3]_3$). Calculated analysis for $\text{C}_{14}\text{H}_{32}\text{OSn}$: Sn, 35.42; found: Sn, 35.38, 35.3.

4′-(11-*Trimethyltin(undecyloxybenzaldehyde*. A mixture of 11-trimethyltinundecan-1-ol (10.1 g, 0.03 m) and pyridine (9.5 g, 0.12 mol) was cooled to 10°C and *p*-toluensulfonyl chloride (6.29 g, 0.033 mol) was added in portions to keep the temperature less than 10 °C. The reaction mixture was stirred 2.5 h, then quenched in ice/HCl (50 g, 15 ml), and extracted with chloroform; the extract was washed with saturated sodium carbonate solution followed by water, and dried over sodium sulfate and stripped to an oil (14.2 g, 0.03 mg >99%); IR indicated no OH but a new doublet at 1195, 1183 cm^{-1} (tosylate).

The tosylate from above (14.2 g) was added to a solution of potassium 4-formylphenoxide (9.6 g, 0.060 mol, in 70 ml of diglyme) and reacted at 40 °C overnight (12 h). 400 ml of water were added and the organic layer extracted with ethyl ether. The ether extract was washed with a 5% sodium hydroxide solution (400 ml × 1), water (400 ml × 4), and a saturated sodium chloride solution (400 ml × 1). The organic layer was dried over anhydrous sodium sulfate and the solvents stripped at low pressure (0.5 Torr), yielding 4′-(11-trimethyltin)undecyloxybenzaldehyde (11.9 g, 0.028, 93%) IR (cm^{-1}) neat, 1680 (C=O), 1600, 1500 (aromatic), 1265, 1020 (aryl–O–C).

4-(11-*Trimethyltin)undecyloxybenzylidene*-4′-*n*-*butylaniline* (Sn-UBBA). Equal molar amounts of the 4′-(11-trimethyltin)undecyloxybenzaldehyde and 4-*n*-butylaniline were refluxed in ethanol for 1.5 h in contact with 4 A molecular sieves (10 g/ℓ/mol of 4-substitutedbenzaldehyde). The reaction mixture was filtered hot, cooled, and the precipitated product recrystallized from ethanol to give the title compound. pmr and analytical data were consistent; thermal data are available as in Fig. 1.

4-(11-*Trimethyltin)undecyloxybenzylidene*-4′-*n*-*octylaniline* (Sn-UBOA). This was prepared in an exactly analogous manner from 4-*n*-octylaniline.

4-(12,12-Dimethyl)tridecyloxybenzylidene-4′-*n*-alkylanilines. (The carbon analogs of Sn-UBBA and Sn-UBOA.)

12,12-*Dimethyltridecyl bromide*. 1-Chloro-2,2-dimethylpropane (25 g, 0.235 mol) in 100 ml of dry tetrahydrofuran was added slowly to dry magnesium (5.7 g, 0.235 eq.) under nitrogen while maintaining reflux. A few drops of methyl iodide was added to initiate the reaction. After refluxing overnight, the solution was added to a cooled (less than 10 °C) mixture of 1,10-dibromodecane (70.5 g, 0.235 mol, 100 ml dry tetrahydrofuran) and dilithium tetrachlorocuprate [1.0 ml, prepared by the addition of (0.848 g, 0.02 mol) lithium chloride and 1.34 g, 0.01 mol) of anhydrous, copper II chloride (Alfa Inorganics) to 100 ml of dry tetrahydrofuran and stirred until dissolved] while maintaining the temperature below 10 °C during the addition. The reaction mixture was stirred an additional 3 h (reaction temperature <10 °C) followed by the addition of 300 ml of ethyl ether and 110 ml of a saturated ammonium chloride solution. Enough water was added to dissolve the inorganic salts which precipitated. The organic layer was separated and washed with water and a saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After stripping, distillation could not adequately separate the products of the reaction, shown by gas chromatographic analysis (program rate 128°–240 °C/8 °C/min) to contain 1,10-dibromodecane (retention time, 8.7 min), 12,12-dimethyltridecylbromide (retention time, 9.3 min), and 2,2,15,15-tetramethylhexadecane (retention time, 10.0 min). This mixture was used directly.

12,12-*Dimethyltridecyloxybenzaldehyde.* The potassium salt of 4-hydroxybenzaldehyde (24 g, 0.150 mol) and 14.7 g of the above mixture containing 12,12-dimethyltridecylbromide were added to 200 ml of diglyme and reacted at 50° for 12 h. Ether (400 ml) was added to the cool reaction mixture and the organic layer washed successively with water, 5% sodium hydroxide, water, and saturated sodium chloride solution, then dried over sodium sulfate. After stripping, a solid suspended in a liquid remained. The solid proved to be 1,10-bis(4-formylphenoxy)decane and was removed by filtering. The liquid was distilled and gave two fractions; the first (bp 108°–114°/0.07 Torr) was 2,2,15,15-tetramethylhexadecane (3.8 g, 0.014 mol) and the second fraction (bp 171°–174°/0.025 Torr) was the desired product (8.3 g, 0.025 mol, 44%) ir (neat) cm^{-1}, 1680 (CHO), 1600, 1500 (aromatic), 1265, 1017 (aryl–O–C), 1395, 1365 [$-C(CH_3)_3$]. (pmr) ($CDCl_3$)δ, 8.97 (*s*, 1, CHO), 6.70 (A_2X_2, 4, $J = 8.0$ Hz, aromatic), 3.65 (*t*, 2, $J = 6.0$ Hz, aryl–O–CH_2–), 1.34–1.02 [broad singlet, 20, $-(CH_2)_{10}-(CH_3)_3$], 0.79 [*S*, 9, $C(CH_3)_3$]. Mass spectrum (70 eV) m/z (relative intensity) 332 (M^+, 4.4), 331 (M^+-H, 16.7), 317 (M^+-CH_3, 7.8), 275 [M^+-$C(CH_3)_3$, 4.4].

4-(12,12-Dimethyl)tridecyloxybenzylidene-4′-*n*-pentylaniline and the 4-*n*-octylaniline derivatives were prepared in a manner similar to the preparation of the analogous tin-containing anils. The analysis for the 4-*n*-octylanil was typical and is given below:

p-(12,12-*Dimethyl*)*tridecyloxybenzylidene-p′-n-octylaniline.* NMR ($CDCl_3$)δ, 8.41 (*S*, 1, –CH=N), 7.40 (A_2X_2, 4, $J = 8.5$ Hz, aromatic), 7.16 (*S*, 4, aromatic), 4.02 (*t*, 2, $J = 6.0$ Hz, aryl–O–CH_2–), 2.63 (*t*, 2, $J = 7.0$ Hz, aryl–CH_2–), 1.30 [broad singlet, 35, aryl–C–C_7H_{15}, aryl–O–C–$(CH_2)_{10}$–], 0.87 [*S*, 9, $-C(CH_3)_3$].

Calculated analysis for $C_{36}H_{57}NO$: C, 83.18, H, 11.05 N, 2.69. Found values: C, 83.20, H, 10.96, N, 2.71.

Mossbauer samples

Sn-UBBA and Sn-UBOA were studied in pure form. The pure samples were prepared by heating these compounds in vacuum to about 90 °C for 5–10 min and then pouring them into a 1 mm thick washer, 11 mm in diameter. The other liquid crystals were studied with the help of Sn-bearing probe compounds dissolved in the liquid crystal under study. Thus samples of 8.05% Sn-UBBA dissolved in TBPA and of 8.31% Sn-UBOA in TBOA (both with sample diameter equal to 7 mm and sample thickness equal to 3.2 mm) were used for the study of TBPA and TBOA.

The peculiar dimensions and compositions of the last two samples are due to the fact that the available quantities of TBOA and TBPA were very small (less than 0.2 g). The system under study was sandwiched between mylar windows.

The solutions were prepared by heating a known mixture of the solute and the liquid crystal under study, in vacuum at a temperature 10 to 15 °C higher than the clearing point of the liquid crystal, for 4 to 5 h. The dissolution was facilitated by shaking the sample several times during the above time interval.

It is very important to be sure that the binary systems were homogeneous solutions. To check the homogeneity of the solutions, the following were done. (a) The transition temperatures of the pure liquid crystal and those of the solutions were compared through microscopic observations of the samples under crossed polarizers on the hot stage of a Reichert NR 382013 polarizing microscope. For small concentrations of the solute, a homogeneous solution should exhibit the same transitions as the pure liquid crystal. As expected, these transitions occurred at slightly lower temperatures than their pure liquid crystal counterparts and they were not as sharp. (b) DSC scans of the samples were taken on a Perkin-Elmer DSC-2 differential scanning calorimeter,[8] to check the phase transition temperatures. (c) X-ray photographs (Laue patterns) of the samples at room and higher temperatures were taken with a Picker 816E x-ray generator.

The x-ray photographs of the first three samples which were taken at room temperature immediately after cooling from the isotropic phase (with a 45 min exposure time) indicated that these samples were in a supercooled smectic *B* phase. The x-ray photographs of the fourth sample (Sn-UBOA in TBOA) showed a definite crystalline x-ray pattern. Since an x-ray photograph of this sample taken at 60 °C did not show any sign of crystallization, it was assumed that the crystalline pattern observed in x-ray pictures of this sample taken at room temperature was due to its crystallization during the time required for cooling and x-ray exposure. The DCS scans of this sample taken with a cooling rate of 10 °C/min did not show crystallization during the cooling process from 400 to 240 K.

The lowest temperature liquid crystalline phase of Sn-UBBA has been studied by de Vries.[9] Using the second-order inner ring of the Laue patterns of this compound, he found that the interlayer distance is 34.70 Å. The molecular length obtained from a space filling model is 35 Å. The small difference between the two lengths implies that this is a normal phase. In addition, the outer ring, though not very sharp, is definitely single. Thus, this phase of Sn-UBBA has been identified as normal smectic *B*.

The alignment of the samples was achieved by heating them to the isotropic phase in an oven made from an aluminum block. The heating element was a 60 Ω wire resistor wound bifilarly around the block. The oven was placed in the air gap of a 9 in. Varian magnet (pole gap width 2.7 in.). There the angle θ between the normal to the sample surface (which coincides with the direction of the γ-ray beam during the Mossbauer run) and the direction of the magnetic field could be set with an accuracy of ±0.5°. The sample of pure Sn-UBBA used for orientational studies at 77 K was aligned with a 10 in. Magnion magnet. After the sample was kept at about 10–20 °C above its clearing point for about 15 min, it was slowly cooled to room temperature. The magnetic field was turned off and the sample removed from the magnet attached to the sample support rod and inserted into the Andonian Mossbauer absorber cryostat. All the 77 K data were obtained from samples cooled by direct immersion of the sample into the liquid nitrogen contained in the sample chamber of the cryostat; the cooling process was completed in about 2 min.

Data reduction

Figure 2 shows the transmission spectra of the glassy phase of pure Sn-UBBA at 90 K, aligned in a 9 kG field, for $\theta = 0°$ and $\theta = 90°$. As expected from the near tetrahedral symmetry around the tin atom, the spectra are apparent singlets. Similar spectra are obtained for the other samples mentioned above. The Mössbauer spectra of all the samples were fitted with a single Lorentzian line with the help of the computer program PARLORS MF,[10,11] using a Burroughs 6800 computer. The points plotted in all the figures represent the averages of many determinations of the respective physical quantity. For example, at least four measurements were used in the case of pure Sn-UBBA aligned in 9.15 kG with a maximum of ten points for each of the $\theta = 0°$ and $\theta = 90°$ orientations. At least two determinations were used in the case of the same sample aligned in 10.2 kG, and at least three determinations were used for the rest of the samples.

To determine a measure of the errors in all the 77 K data, the following procedure was used: first, the mean absolute deviation from the mean value of that quantity was calculated for each orientation of the liquid crystal; then the average value of these numbers was taken to represent an "error measure" of the data. Half the length of the error bars for these data is equal to this "error measure."

In the analysis of the Sn-UBBA data, the absolute fraction of the source and the linewidth of the source in the zero thickness limit was required. For the determination of these parameters, we used the method of Shirley *et al.*[12] According to these authors, the areas under the Mössbauer peak (for a single line spectrum) is given by the formula

$$(\text{Area})_{\text{cm/s}} = \pi f_{\text{exp}} v_a = \pi v_a f[1 - \exp(-\tfrac{1}{2}t) I_0(\tfrac{1}{2}t)] , \qquad (1)$$

where f_{exp} is the experimental relative peak height, v_a is the apparent (experimental) halfwidth measured in cm/s, f is the absolute fraction of the source, t is the Mössbauer thickness of the absorber, and I_0 is the zero-order Bessel function of the imaginary argument. t is given by the relation

$$t = n_0 \sigma_0 f'(\Gamma/\Gamma') . \qquad (2)$$

Here n_0 is the number of the Mössbauer nuclei per cm^2 of a cross section of the sample normal to the γ-ray beam, σ_0 is the nuclear cross section at resonance, Γ is the natural linewidth, and Γ' is the linewidth of the absorber in the zero thickness limit. From Eq. (1),

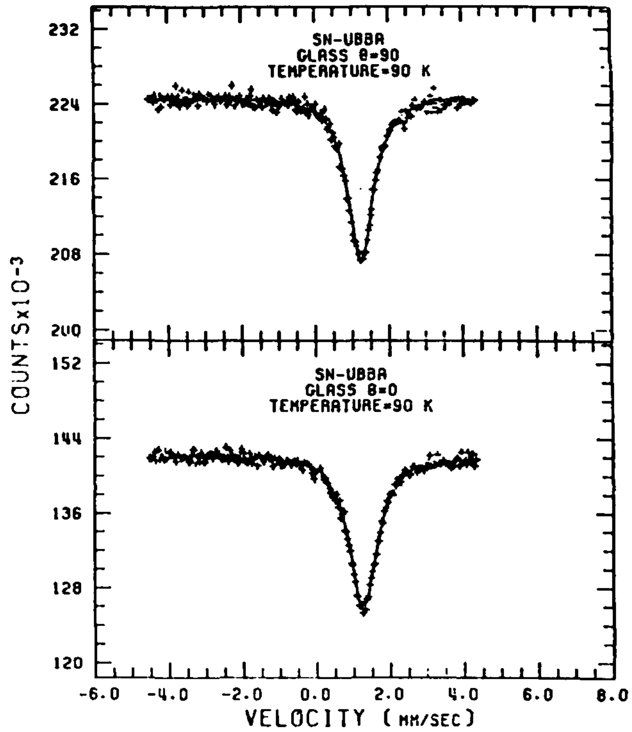

FIG. 2. Mössbauer spectra of pure Sn-UBBA in the glass phase, at 90 K, and for the orientation angles $\theta = 90°$ for the upper and $\theta = 0°$ for the lower spectra, respectively. The sample was aligned by cooling from the melt in a 9 kG magnetic field.

$$f_{\text{exp}} = f[1 - \exp(-\tfrac{1}{2}t) I_0(\tfrac{1}{2}t)] . \qquad (3)$$

Γ' can be derived from the variation of the apparent (experimental) linewidth Γ_a with the absorber thickness t. According to Ref. 12, a good approximation is given by the relation

$$\Gamma_a = (\Gamma_s + \Gamma')(1 + 0.135t) , \quad 0 \le t \le 5 , \qquad (4)$$

where t is given by Eq. (2) and Γ_s is the linewidth of the source in the zero thickness limit.

In order to determine the absolute Mössbauer fraction for the 23.8 keV ^{119}Sn radiation from the CaSnO$_3$ source which was used in this work, Mössbauer spectra were taken for a series of nine natural tin absorbers which consisted of a different number (the thinnest of 1 and the thickest of 9) of identical tin foils, at 90 K. Each foil had a mass 14.0±0.1 mg, a thickness of 0.005 in., and an area with a 10.608 mm diam exposed to the γ-ray beam. The CaSnO$_3$ source had a diameter of 16 mm. The manufacturer provided the source half-width of $\Gamma_s/2 = 0.1715$ mm/s.[13] Using this value for Γ_s, one can get Γ' and f' by fitting the half-widths versus thickness data to Eq. (4). The fitting resulted in $\Gamma'/2 = 0.2558$ mm/s and $f' = 0.374$.

The above value of Γ' and the experimental relative peak heights, multiplied by a background correction factor, were used to fit Eq. (3) to the experimental data. To determine the background correction factor, spectra were obtained at 90 K from the single foil sample with both a 2 mil Pd filter and a 4 mil Pd filter covering the $CaSnO_3$ source. For a 4 mil Pd filter, one should expect that approximately 98% of the background radiation is removed from the γ-ray beam.[13] We found that, at 90 K, for natural tin absorbers

(Background correction factor)

$$= \frac{A(4 \text{ mil Pd})}{A(2 \text{ mil Pd})} = 1.1528 \ . \qquad (5)$$

The fitting gives $f = 0.440$ and $f' = 0.453$. There is a difference in the values of f' as derived by fitting Eq. (4) to the experimental linewidths versus thickness data and the value of f' as derived by fitting Eq. (3) to the experimental relative absorption versus thickness data. One reason for this discrepancy is the fact that the formulas used in these calculations are only approximately correct. Another is the fact that β tin has a small quadrupole splitting[14] and this will affect the results. Also, small uncertainties exist in the experimental data and the background correction factor. The resulting value of f is in the region expected by the manufacturer of these sources.[13]

THE VARIATION OF THE PERCENT EFFECT, THE MEAN SQUARE VIBRATIONAL AMPLITUDE OF THE Sn NUCLEI, AND THE LINEWIDTH VERSUS θ

The data involving the θ dependence of the percent effect for the pure samples were first analyzed using the small thickness approximation. In this approximation the total area under the Mössbauer absorption peak is taken to be proportional to the absolute fraction of the absorber under study. Also in this case, because of the nearly tetrahedral symmetry around the Sn atom, we assumed that the intramolecular contribution to the vibrational anisotropy was very small.

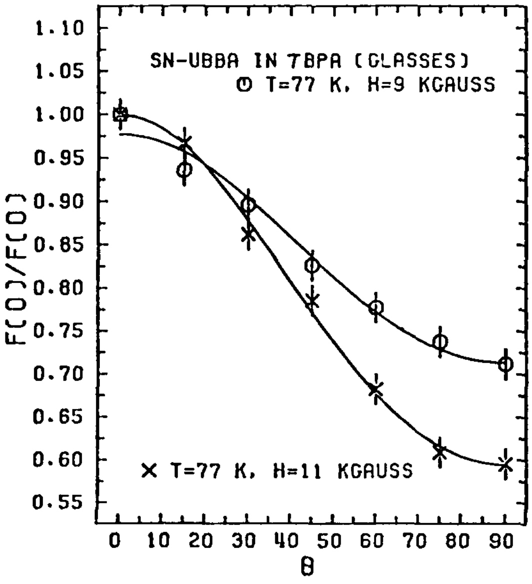

FIG. 3. The variation of the reduced area under the Mössbauer peak vs θ for an 8.05% solution of Sn-UBBA in TBPA aligned in 9 and 11 kG. The continuous lines represent the best fit of Eq. (6) to the experimental data. The results of the fit are given in Table I.

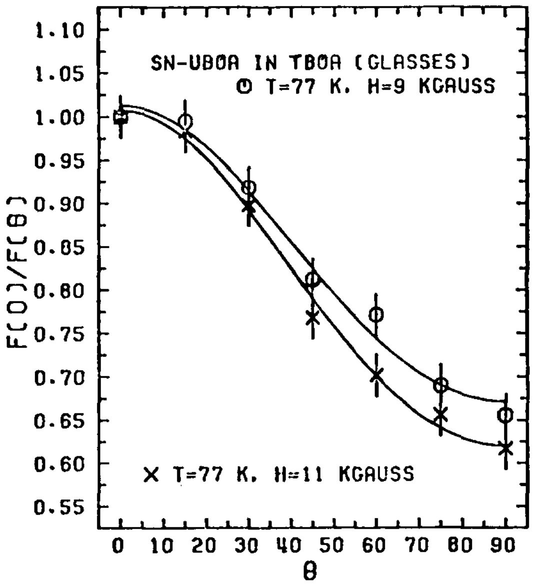

FIG. 4. The variation of the reduced area under the Mössbauer peak vs θ for an 8.31% solution of Sn-UBOA in TBOA aligned in 9 and 11 kG. The continuous lines represent the best fit of Eq. (6) to the experimental data. The results of the fit are given in Table I.

As can be seen from Figs. 3–5, the variation of the reduced absorption intensity (area under the peak) of the Mossbauer spectra (normalized with respect to its value at $\theta = 0°$), of the glassy phase of our samples, at 77 K, vs θ is well represented by the equation[15]

$$\frac{f'(\theta)}{f'(0)} = \exp(\epsilon_L \sin^2\theta) + C \ . \qquad (6)$$

Here, $f'(\theta)$ is the percent effect when the director forms an angle θ with the direction of the γ-ray beam (which coincides with the normal to the flat surfaces of the sample), ϵ_L is the lattice contribution to the nuclear vibrational anisotropy, and C is a constant which accounts for the fact that in the reduction of the experi-

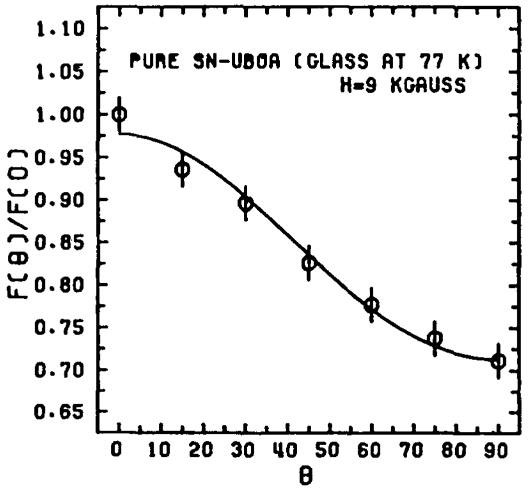

FIG. 5. The variation of the reduced area under the Mössbauer peak vs θ for pure Sn-UBOA aligned at 9 kG. The continuous line represents the best fit of Eq. (6) to the experimental data. The results of the fit are given in Table I.

TABLE I. ϵ_L, C, and Γ' are given for various samples and field strengths. α_A and α_H are the values of α which result from fitting the corrected area (A) vs θ data and the experimental half-widths vs θ, respectively. tively.

Sample	Magnetic field (kG)	ϵ_L	C	Γ' (mm/s)	α_A	α_H
Sn-UBBA	9.15	−0.49 ± 0.01	···	0.4324	2.980	2.800
Sn-UBBA	10.2	−0.51 ± 0.01	···	0.4216	3.016	2.747
Sn-UBOA	9	−0.31 ± 0.01	−0.023	···	···	···
8.05% Sn-UBBA in TBPA	9	−0.45 ± 0.01	−0.006	···	···	···
8.05% Sn-UBBA in TBPA	11	−0.52 ± 0.01	−0.0001	···	···	···
8.31% Sn-UBOA in TBOA	9	−0.43 ± 0.01	0.014	···	···	···
8.31% Sn-UBOA in TBOA	11	−0.49 ± 0.01	0.007	···	···	···

mental data, $f'(0)$ was assumed to be known very well (with zero uncertainty). Here, ϵ_M, the molecular contribution to the vibrational anisotropy, is taken to be zero. Strictly speaking, it is easy to see that C is slightly θ dependent but that one can, at a small risk, replace the function $C(\theta)$ with a constant C. The results of fitting this equation to the reduced absorption intensity versus θ data are given in Table I.

As can be seen from Figs. 3 and 4, the orientation data depend on the different intensities of the aligning magnetic field. This field dependence is due to the fact that the sample layers adjacent to the sample boundaries are misaligned because boundary forces cause surface alignment which influences the liquid crystal molecules to a non-negligible depth. The thickness of this boundary layer is field dependent and it decreases for higher values of the field.[2,16] Thus the experimental Mössbauer spectrum of these samples is the result of mixing γ-ray absorptions from the well-aligned and the misaligned regions. The application of Eq. (6) to these data results in different effective values of ϵ_L for data taken from samples aligned in different magnetic fields.[2,16] Since the approach to full alignment is an asymptotic function of the field, one can either quote the values of ϵ_L, determined in the above way as lower limits of their true value, or say that they represent their true value if the error is small enough. Even with the presence of the misalignment, the conclusions of Ref. 15 in which ϵ_L values are compared are still valid since all the experiments were performed on very similar liquid crystalline glasses (the only difference resulted from the use of different solutes), which were aligned and cooled under the same conditions.

As can be seen from Figs. 6 and 7, the linewidths for the solutions are rather independent of θ. In con-

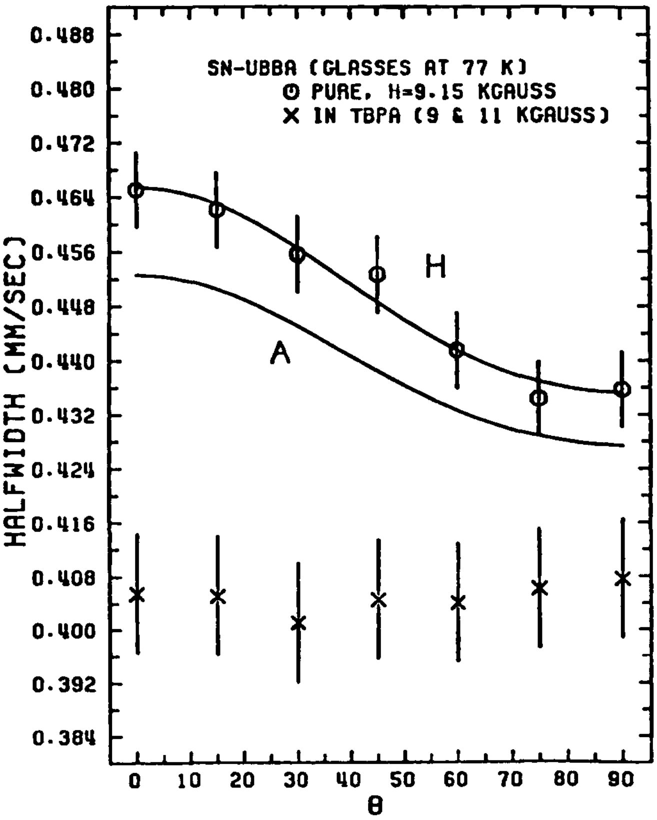

FIG. 6. The variation of the half-width vs θ for pure glassy Sn-UBBA and the 8.05% solution of Sn-UBBA in TBPA. The spectra were taken at 77 K. For the meaning of the continuous curves A and H, see the text.

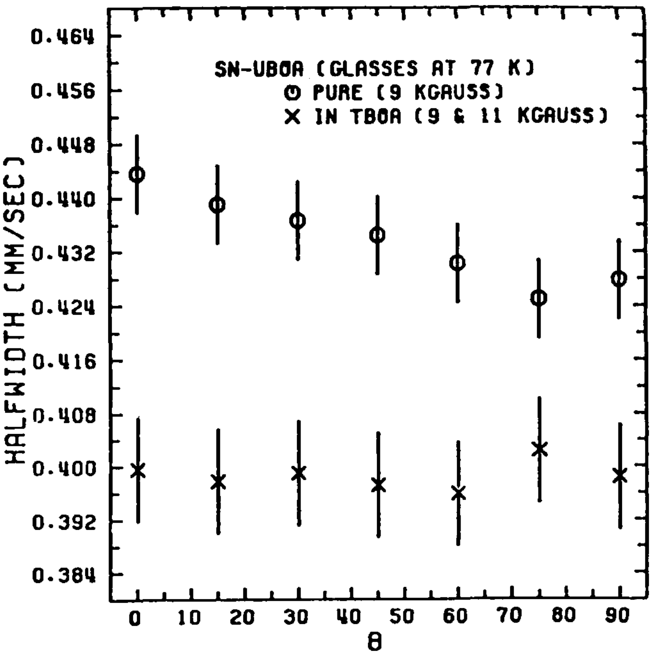

FIG. 7. Comparison of the half-width vs θ variation for our samples of pure Sn-UBOA and 8.31% solution of Sn-UBOA in TBOA.

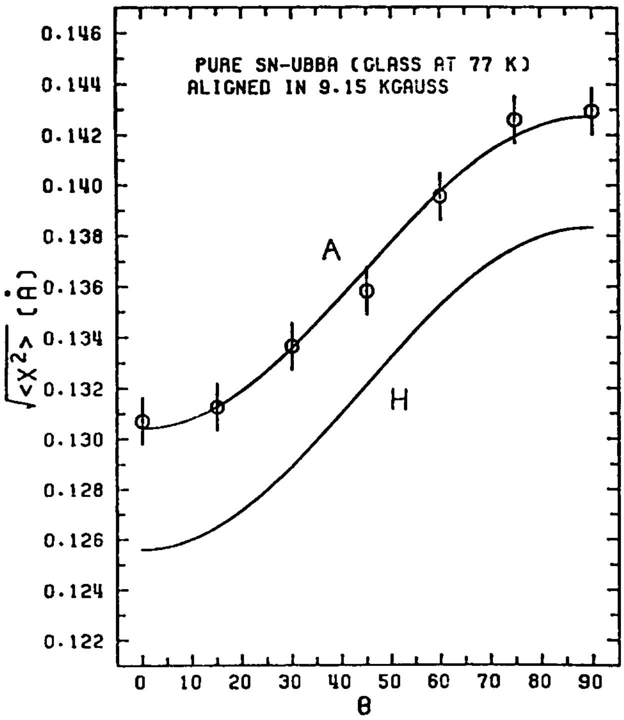

FIG. 8. The variation of $\sqrt{\langle x^2\rangle}$ vs θ for pure glassy Sn-UBBA aligned in a 9.15 kG magnetic field. The spectra were taken at 77 K. For the meaning of the continuous curves A and H, see the text.

trast, the linewidths of the pure Sn-bearing liquid crystals show a very pronounced angular dependence. The statistics for these data do not leave any ambiguity as to the fact that this variation is real. Since the most apparent difference between the pure Sn-bearing liquid crystals and the solutions is the greater thickness (in mg/cm^2 of Sn^{119}) in the pure Sn-bearing liquid crystals, one can easily conclude that the linewidth versus θ variation in the pure liquid crystal is due to the fact that the small thickness approximation fails for these samples.

For thick absorbers the apparent experimental linewidth Γ_a is given by Eq. (4). In the case of liquid crystalline glasses of both pure Sn-UBBA and pure Sn-UBOA, the absolute Mossbauer fraction is given by the relation

$$f'(\theta) = \exp(-\alpha - \epsilon_L \cos^2\theta) \ . \qquad (7)$$

Thus

$$\Gamma_a = (\Gamma_s + \Gamma')\,[1 + 0.135 n_0 \sigma_0 (\Gamma/\Gamma') \exp(-\alpha - \epsilon_L \cos^2\theta)] \ . \qquad (8)$$

Equation (8) connects the variation of the experimental (apparent) linewidth Γ_a vs θ with the quantities Γ', α, and ϵ_L. Since we cannot derive reliable values for Γ', α, and ϵ_L by fitting Eq. (8) to the experimental Γ_a vs θ data, we instead proceeded in the following way.^{2} An approximation of ϵ_L was obtained from the $f'(\theta)/f'(0)$ vs θ data using Eq. (6). Using this value of ϵ_L, Eq. (8) was fitted to the experimental half-width versus θ data with adjustable parameters Γ' and α. The resulting value of Γ' was inserted into Eq. (3) with the measured intensities of the Mössbauer spectra. A first approximation to the absolute fractions for each value of θ for which we had experimental data was thus obtained. Fitting Eq. (7) to these values of the absolute fractions yielded a new set of values of α and ϵ_L. Before proceeding further, the new values of α and ϵ_L were checked to determine whether they agreed with the initial values without 0.004. This procedure was repeated until the last condition was met.

Finally, a value of ϵ_L, a value of Γ', and two values of α [the first resulting from the fit of Eq. (8) to the experimental half-width versus θ data and the second from the fit of Eq. (7) to the values of the absolute fraction as derived from Eq. (3)] are obtained. The results of the analysis are given in Table I. One also gets two sets of values for the absolute fractions: (a) from the areas under the Mössbauer peak and (b) from the experimental half-widths. The results of the fit for the case of Sn-UBBA are shown in Figs. 6 and 8. In Fig. 8, the "experimental" points are derived from the areas under the Mössbauer peak, corrected for the background. The continuous line A was generated from Eq. (7) [if we take into account that $f' = \exp(-1/\bar{\lambda}^2 \langle x^2\rangle)$], assuming that the correct value of α is the one derived from the areas. The continuous line H was generated in the same way as line A assuming that the correct value of α is the one derived from the half-widths. Figure 6 was generated in a similar way. The continuous line H was generated from Eq. (8) assuming that the correct values of f' are the ones derived from the experimental half-widths, while in the generation of curve A from Eq. (8) we assumed that the correct values of f' were the ones derived from the areas under the peak.

That the curves A and H in Fig. 8 do not match completely is to be expected because (a) spectrometer parasitic vibrations are expected, (b) there is some error in the background subtraction, (c) the imperfect γ-ray beam collimation could introduce a ~2% to 3% error, and (d) the existence of an unresolved doublet could also introduce an error. Nevertheless, the values of ϵ_L derived with this method are an improvement over the ones which could be derived by just fitting Eq. (6) to the normalized area versus θ data. An alternative way could be to study the effect of the thickness on the experimental half-width as we did for natural tin and to derive Γ' from the resultant data in the same way as we did for natural tin. But we do not believe that we could get any substantial improvement of our results by using the last method. We also demonstrated that the variation of the experimental linewidth versus θ for our Sn-UBBA sample was, in fact, due to the variation of the Mössbauer thickness of the sample because f' is a function of θ. We also derived $\langle x^2\rangle$ and the Debye temperatures θ_D in the high temperature approximation, i.e., using the formula

$$f' = \exp(-6RT/K_B\theta_D^2) \ , \qquad (9)$$

where R is the recoil energy of the emitting nucleus, K_B is the Boltzmann constant, and T is the absolute temperature of the sample (77 K in this case). The assumption is made that the recoiling mass is equal to the mass of the entire probe molecule, as is usually done for molecular crystals.^{17} The results are given in Tables II and III.

TABLE II. The $\sqrt{\langle x^2\rangle}$ and Debye temperatures θ_D for various orientations of pure Sn-UBBA. All spectra were taken at 77 K. The sample was aligned in a 9.15 kG field. The $\sqrt{\langle x^2\rangle}$ were derived from the coupled fit of the experimental areas under the Mössbauer peak and the experimental half-widths.

	From the half-widths.		From the areas	
θ	$\sqrt{\langle x^2\rangle}$ Å	θ_D K	$\sqrt{\langle x^2\rangle}$ Å	θ_D K
0	0.1255	35.32	0.1304	33.99
15	0.1264	35.07	0.1312	33.78
30	0.1288	34.41	0.1335	33.20
45	0.1321	33.55	0.1366	32.45
60	0.1352	32.78	0.1397	31.73
75	0.1375	32.24	0.1419	31.24
90	0.1383	32.05	0.1427	31.10

A comparison of the values of ϵ_L in Table I shows that the values for samples aligned in the higher fields are very close to each other, as one would expect for similar compounds. The introduction of Sn-bearing probe molecules into the non-Sn bearing liquid crystalline structures does not distort their structures significantly and thus their dynamic properties remain the same as for the pure compounds.

The value of ϵ_L for pure Sn-UBOA is low compared to the other samples. Possible reasons for this are (a) the incomplete alignment of the sample (higher fields are probably necessary for the full alignment of this sample) and (b) the fact that the value of ϵ_L listed in Table I was determined by fitting the $f'(\theta)/f'(0)$ vs θ data to Eq. (6), while the variation of the half-width versus θ for this sample indicates that it would be more appropriate to use the same procedure used for pure Sn-UBBA. This was not possible for Sn-UBOA because n_0 was unknown. If the Sn-UBBA data were treated in a manner similar to the pure Sn-UBOA data, the value of ϵ_L would be equal to -0.42 for the Sn-UBBA sample which was aligned in 9.15 kG and -0.44 for the one aligned in 10.2 kG.

It is important to note that the values of ϵ_L in Table I which refer to the solutions which were aligned in 9 kG are very close to the value of $\epsilon_L = -0.45$ of the solution of 4-trimethyltin-benzylidene-4′-*n*-butylaniline (Sn-BBA) in 4-*n*-butoxybenzylidene-4′-*n*-octylaniline (BBOA or 40.8).[15] This sample was assumed in Ref. 15 to simulate the order of the smectic *B* liquid crystalline glass better than the other two samples studied in that work. Also in Ref. 18, it was found that for this sample the orientational order parameter equalled 0.48, the highest measured by the Mössbauer technique. Although comparing ϵ_L for different samples could be dangerous due to the different saturation fields necessary for each compound, the similarity is striking.

The apparent line positions

For pure Sn-UBBA and Sn-UBOA, the line position (LP) of the apparent singlet spectrum (at 77 K) showed a shift towards lower velocities as the orientation angle θ was varied from $\theta = 0°$ to $\theta = 90°$. This variation is quite small even for Sn-UBBA, which is the most pronounced case (see Fig. 9). In this case, the variation is approximately equal to 0.015 mm/s. Also, one can see a similar trend in the θ dependence of the line position for pure Sn-UBOA (Fig. 10), and to a lesser degree for the solutions of 8.05% Sn-UBBA in TBPA (Fig. 9) and 8.31% Sn-UBOA in TBOA (Fig. 10). Because the points corresponding to samples oriented in 9 and 11 kG intermingle, only the averages of all the points for each orientation are plotted in this work. The LP vs θ variation was observed both at the beginning and at the end of each series of measurements, thus excluding the partial decomposition of the samples as an explanation of the effect.

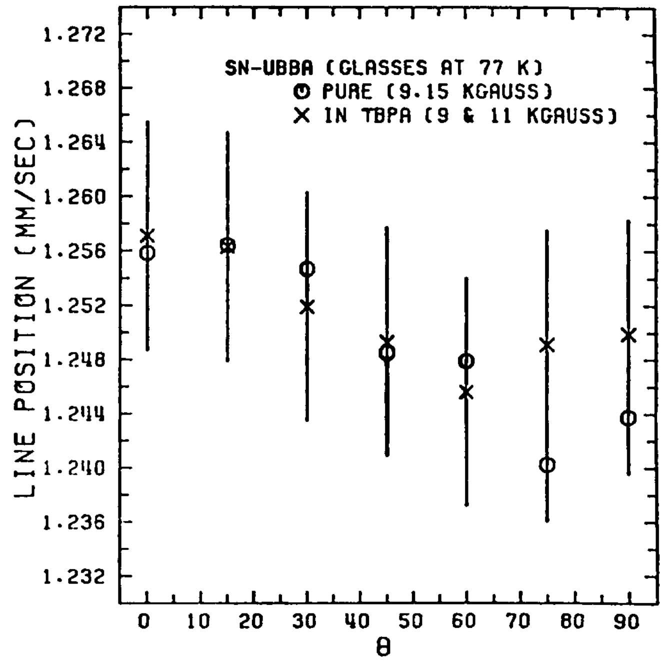

FIG. 9. The θ dependence of the apparent line position of pure Sn-UBBA aligned in 9.15 kG, compared to that of an 8.05% solution of Sn-UBBA in TBPA. The points plotted represent a weighted average of points from spectra of the latter sample when it was aligned in 9 or 11 kG. All spectra were taken at 77 K.

TABLE III. The $\sqrt{\langle x^2\rangle}$ and Debye temperatures θ_D for various orientations of pure Sn-UBBA. All spectra were taken at 77 K. The sample was aligned in a 10.2 kG field. The $\sqrt{\langle x^2\rangle}$ were derived from the coupled fit of the experimental half-widths.

	From the half-widths		From the areas	
θ	$\sqrt{\langle x^2\rangle}$ Å	θ_D	$\sqrt{\langle x^2\rangle}$ Å	θ_D
0	0.1236	35.86	0.1308	33.89
15	0.1245	35.60	0.1317	33.66
30	0.1270	34.90	0.1341	33.05
45	0.1304	33.98	0.1372	32.31
60	0.1337	33.15	0.1405	31.55
75	0.1361	32.57	0.1427	31.11
90	0.1370	32.35	0.1435	30.89

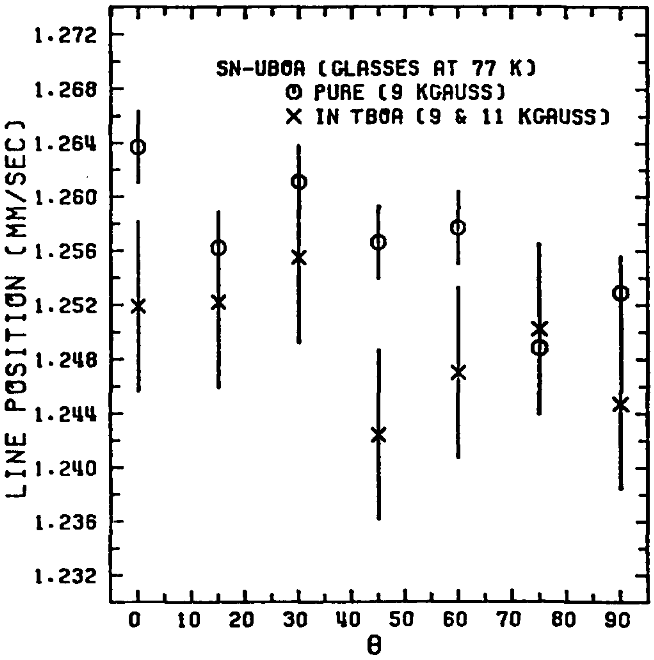

FIG. 10. The θ dependence of the apparent line position of pure Sn-UBOA aligned in 9 kG, compared to that of an 8.31% solution of Sn-UBOA in TBOA. The points plotted represent a weighted average of points from spectra of the latter sample when it was aligned in 9 or 11 kG. All spectra were taken at 77 K.

The LP vs θ variation can be attributed to the existence of an unresolved quadrupole doublet in the spectra of Sn-UBBA and Sn-UBOA. Since in this case the LP tends to lower velocities as θ increases from 0° to 90°, the data would yield $\Delta E_Q > 0$ and thus $V_{zz} < 0$. The negative V_{zz} is opposite to that found for Sn-BBA.[18,19] This result is not unrealistic since a Sn–C bond for a carbon atom in a benzene ring as in Sn-BBA differs significantly from one in a long aliphatic chain.

The fact that the LP vs θ variation is more pronounced in the case of pure Sn-UBBA than the other samples reported herein might be attributed to the comparatively better alignment of Sn-UBBA. This alignment, however, fails to account for data from the solutions of these compounds in TBPA and TBOA since their ϵ_L is similar to the ϵ_L in pure Sn-UBBA (which implies similar alignment if one assumes that in each well-ordered smectic plane of both pure Sn-UBBA and its solution in TBPA, there exists the same ϵ_L). Another reservation is the following: if we assume similar order in each smectic plane and similar alignment of the whole sample for pure Sn-UBBA and its solution in TBPA and if we assume that the LP vs θ variation in these samples is due to the existence of an unresolved quadrupole doublet, then, since the sample of Sn-UBBA used in this work was in the Mössbauer notion (mg ^{119}Sn/cm^2) thicker and geometrically thinner than for Sn-UBBA in solution, the LP vs θ variation of pure Sn-UBBA must be less than for its solution in TBPA.[2] For the same reason, the LP vs θ variation of Sn-UBOA must be smaller than for its solution in TBOA. Clearly, the LP variation for the pure compounds is greatest so, based on differences in alignment, this view must be rejected.

Another factor which can affect the apparent line position is interference. As already mentioned, the Mössbauer thickness of an aligned liquid crystalline glass changes as θ varies from 0° to 90°, since the absolute fraction of the absorber is a function of θ. Erickson *et al.*[20] found that in the case of ^{197}Au, for which a dispersion coefficient $\xi = (-4.14 \pm 0.17) \times 10^{-3}$ was derived, the LP varied by 3.3×10^{-3} (mm/s)/(unit t_A), where t_A is the Mossbauer thickness of the absorber. According to Mitrofanov *et al.*,[21] in the case of ^{119}Sn, $\xi = (-1.5 \pm 0.5) \times 10^{-3}$. Thus, one would expect the LP in this case to vary by less than the one of ^{197}Au for the same variation of absorber thickness. The thickness variation (caused by the θ dependence of the recoil-free fraction) at 77 K, from $\theta = 0°$ to $\theta = 90°$, for the sample of Sn-UBBA which was aligned in 10.2 kG is 0.912. One expects that the LP vs θ variation due to interference effects should be 0.001 mm/s, which is too small to measure.

That the effect of the thickness on the LP vs θ variation is small can be seen from Fig. 11 where the LP's of pure Sn-UBBA are plotted as a function of temperature for different orientations of the sample.[2,3] It can be easily seen that the difference in LP between the various orientations of the sample is nearly constant from 90 (thick absorber) to 140 K (thinner absorber because f' is smaller).

Although it is certain that a part of the discrepancy is due to the quality of the data, it is possible that the LP vs θ variation is bigger in the pure Sn-UBBA and pure Sn-UBOA glasses because of the presence of the more bulky $-Sn(CH_3)_3$ groups around each $-Sn(CH_3)_3$ group compared to the $-C(CH_3)_3$ groups which surround the $-Sn(CH_3)_3$ groups in the solutions. The pseudotetrahedron around each Sn atom, in the pure Sn-bearing

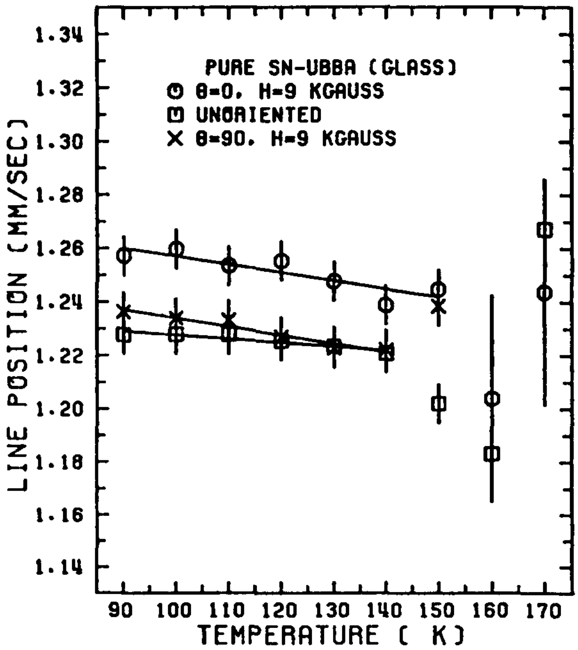

FIG. 11. The line position (mm/s) of the glass of pure Sn-UBBA vs temperature (K) for various orientations of the sample.

compounds, is therefore slightly more distorted. Distortions of even spherical groups dissolved in nematic liquid crystals[22–24] and lyotropic liquid crystals[25] have been observed in high resolution NMR studies. A model of the distortions has been given in Ref. 26. In view of the more or less tetrahedral symmetry around the tin atom, one has to wonder if the quadrupole interaction, even in solutions of Sn-UBBA and Sn-UBOA, is not due to small distortions of the solute molecules by their anisotropic environment.

Because of the small LP vs θ variation in these compounds, we preferred not to perform an anlysis similar to the one of Ref. 18 (see also Ref. 2), which was used successfully in the case of a solution of Sn-BBA in BBOA. It is evident that in the cases of pure Sn-UBBA and Sn-UBOA, one should take into account the effect of the thickness on the LP vs θ variation.[2,18] Such an analysis, however, would consume a tremendous amount of computer time, while the results would be uncertain to within 50% to 100%. The LP vs θ variation for the thick absorber, however, follow patterns which are similar to those for the thin absorber. These cases are considered in detail in Ref. 2.

CONCLUSIONS

Two tin-bearing liquid crystalline molecular systems (Sn-UBBA and Sn-UBOA) were designed and prepared for the purpose of Mössbauer Effect analysis.

Pure Sn-UBBA and pure Sn-UBOA exhibited orientation (θ) dependent linewidths which were accounted for by a variation of the Mössbauer absorber thickness with orientation. In this instance, the thickness variation was caused by the θ dependence of the Mössbauer recoilless fraction. By correcting for the thickness effect, the lattice contribution to the recoil anisotropy ϵ_L, the linewidth in the zero thickness limit and the Debye temperatures for the Sn-UBBA smectic *B* glass were determined.

The data for the smectic *B* glasses of solutions of Sn-UBBA in TBPA and Sn-UBOA in TBOA showed that the values of ϵ_L were nearly the same as for the pure compounds.

In every case, the absence of a nematic phase did not hinder the formation of an aligned glass.

The variation of the apparent experimental singlet line position of Sn-UBBA with orientation was satisfactorily accounted for by noting the presence of an unresolved quadrupole doublet in pure Sn-UBBA.

An analysis of the temperature-dependent Mössbauer data from these systems will be published separately.

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