

## Smectic *B* liquid-crystalline glass (at 77 °K) as seen by the Mössbauer effect of Sn-bearing solute molecules\*

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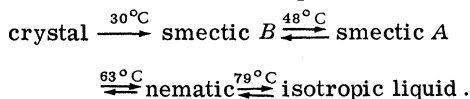
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(Received 30 September 1974; revised manuscript received 4 February 1975)

By observing the orientation dependence of the recoil-free fraction for three Sn-bearing solute molecules, we have determined the lattice contribution of a smectic *B* glass (at 77 °K) to the anisotropy of the nuclear vibrational amplitude for the Sn-119 nucleus. The measured anisotropy depends on the solute shape and length and is explained in terms of the layered smectic structure and the difference between the character of the central core and the end-chain regions of the host liquid-crystal molecules. The resonant line position for the solute, 4-trimethyl-tin-benzylidene-4'-*n*-butylaniline (Sn-BBA), was found to be dependent on the angle ( $\theta$ ) between the preferred direction of the aligned liquid-crystalline glass and the Mössbauer  $\gamma$  beam. We interpret this in terms of an unresolved quadrupole splitting ( $\Delta E_Q$ ) for this molecule. The line-shift data are shown to yield the sign of  $V_{zz}$  and the magnitude of  $\Delta E_Q$  for the Sn-BBA molecule.

### I. INTRODUCTION

Liquid-crystalline phases are distinct states of matter which are separated from the normal liquid and solid phases by first-order phase transitions. The liquid-crystalline material used in this study was 4-*n*-butoxybenzylidene-4'-*n*-octylaniline (BBOA or 40, 8).<sup>1</sup> BBOA possesses three liquid-crystalline phases which are listed below with the transition temperatures:



There are several subdivisions within the nematic and smectic liquid-crystalline designations.<sup>2,3</sup> Nematic liquid crystals are optically uniaxial and possess molecular order in that the molecules orient about some preferred direction. The latter is not unique to nematic liquid-crystalline phases, but the fact that it occurs along with liquidlike molecular mobility in all directions is unique to the nematic phase. All smectics, on the other hand, are characterized by a layered structure in which the molecules maintain their distribution about some preferred direction, but in a way such that their centers of gravity lie in layers. There are many different classifications of smectics which include smectic *A* and smectic *B*. These classifications are determined by the combinations of intraplanar and interplanar translational order which are observed. The general properties of the smectic *A* classification are that they are optically uniaxial and the molecules possess no intraplanar molecular order. Also the preferred molecular direction is parallel to the planar normals. In contrast, the smectic *B* phase

possesses some intraplanar translational order, and de Vries has distinguished three separate types of smectic *B*.<sup>3</sup> The smectic *B* phase of BBOA belongs to the  $B_1$  classification of de Vries, and it is also called the "ordinary *B*." Its characteristics include the following: it is optically uniaxial; the preferred direction of the molecular long axes is perpendicular to the smectic plane; and there is an ordered arrangement of the molecules within the smectic layer.

A further property which distinguishes nematics from all of the smectic classifications is that a nematic phase can be completely aligned with a laboratory magnetic field (1.5–3.0 kG). That is, in the presence of the field, all the nematic molecules distribute themselves about a single preferred direction which is parallel to the magnetic field. Smectics cannot be aligned in this way because of the large energy requirements of reorienting the layered arrangement. However, the smectic phases of liquid-crystalline materials such as BBOA can be aligned by cooling the sample through the nematic-smectic transition in the presence of an external magnetic field.<sup>4,5</sup> Further cooling through smectic-smectic transitions does not disturb the alignment. Therefore, the smectic *B* phase of BBOA can be aligned with the result that all the planar normals are parallel to the molecular preferred direction (as determined by the magnetic field).

In this report we have used the Mössbauer effect to study the lattice anisotropy of the smectic *B* phase of BBOA. To do this we have made use of the above-mentioned alignment properties of liquid-crystalline materials to provide an ordered system for the Mössbauer measurement. The Sn-119 Mössbauer nuclide was incorporated into

the liquid-crystalline system by dissolving a tin-bearing molecule (~3–5 wt %) into the BBOA. Three separate tin-bearing molecules were used in this investigation. They were chosen for varied reasons which will be discussed later, but common to each was the fact that low temperatures (~77 °K) were required to provide a significant probability for a recoil-free event in the absorber. As a result, we used the experimental fact that the only allowed glass phase of BBOA is the smectic *B* glass, because only the solid (crystal)-smectic *B* transition can be supercooled.<sup>6,7</sup> Therefore, after aligning the smectic *B* phase by cooling from the nematic phase in the presence of a 9 kG magnetic field, the sample was rapidly cooled to 77 °K by direct immersion into liquid nitrogen (in the Mössbauer absorber Dewar). In this way an aligned smectic *B* glass was produced such that Mössbauer measurements could be obtained as a function of the angle ( $\theta$ ) between the molecular preferred direction as determined by the external magnetic field and the direction of the Mössbauer  $\gamma$ -ray beam from the Sn-119 source.<sup>4,8</sup>

The three absorber molecules were 4-trimethyltin-benzylidene-4'-*n*-butylaniline (Sn-BBA)  $[(\text{CH}_3)_3\text{Sn}(\text{C}_6\text{H}_4)\text{HCN}(\text{C}_6\text{H}_4)\text{C}_4\text{H}_9]$ , *N,N'*-di- $[p$ -*n*-(3-trimethyl-tin)-propoxybenzylidene]-1',4-phenylenediamine (Sn-PBPD)  $[\{(\text{CH}_3)_3\text{SnC}_3\text{H}_6\text{O}(\text{C}_6\text{H}_4)\text{HCN}\}_2(\text{C}_6\text{H}_4)]$ , and tin tetrabutyl (Sn-TB). They were chosen first of all because they are soluble in BBOA and secondly because they appeared to exhibit single-line Mössbauer spectra. The absence of a quadrupole splitting indicated that the tin atom in each molecule occupied a site of nearly tetrahedral symmetry within the molecule. As a result, we assumed that the molecular contribution to the recoil-free fraction ( $f$ ) was isotropic<sup>9</sup> even though the large solute molecules possess many internal degrees of freedom which may provide for anisotropic intramolecular vibrations of the tin nuclei. In this approximation, which is discussed in detail in Sec. III, we have taken the intramolecular and intermolecular vibrations to be uncoupled, as is usually done for molecular crystals.<sup>10</sup> Thus, the intermolecular contribution to the Sn vibrational anisotropy which results from the layered molecular structure of the smectic *B* glass gives rise to the  $\theta$  dependence of  $f$  for the three solutes. The observed differences in the  $f$ -vs- $\theta$  plots for the three solutes are explained in terms of the differences in solute shape and the differences in character of the central core and the end-chain regions of the host BBOA molecules.

For the Sn-BBA molecule, however, there was an added complication, because its apparent single-line absorption exhibited a  $\theta$ -dependent vel-

ocity shift which was caused by the different  $\theta$ -dependent transition probabilities of each partner of an unresolved quadrupole doublet. That is, in the event of a small but nonvanishing quadrupole splitting, an angular dependence of the centroid of an apparent single-line absorption is a reflection of the different orientational dependencies of the  $\pi$  and  $\sigma$  transition probabilities<sup>11</sup> (for the  $I=\frac{3}{2} \rightarrow I=\frac{1}{2}$  transition). However, the change in line position for the maximum change in orientation (i.e.,  $\theta=0^\circ$  to  $\theta=90^\circ$ ) was only 0.064 mm/sec. Consequently, the assumption, that the molecular contribution to the mean-square vibrational amplitude of the Sn-119 nucleus was isotropic and did not contribute to the orientation ( $\theta$ ) dependence of the Mössbauer  $f$  factor, was presumed valid even for Sn-BBA. As a result, only the layered smectic *B* structure as modified by the presence of the individual solute molecules was assumed to account for the observed recoil anisotropy.

The  $\theta$ -dependent  $f$  data are presented and discussed in detail in Secs. II and III. Particular emphasis is given to the values obtained for the lattice contribution to the vibrational anisotropy ( $\epsilon_z$ ). The measured values are solute dependent and they are discussed in terms of the structure of the liquid-crystal molecules.

As we have mentioned, the line position of the apparent single-line absorption from the Sn-BBA solute was found to be  $\theta$  dependent. This indicates that there is an unresolved quadrupole split doublet caused by a deviation from the tetrahedral symmetry about the tin in the Sn-BBA molecule. By making some reasonable assumptions about the molecular order and linewidth which are based upon measurements on other solutes in both BBOA and 4-*n*-hexoxybenzylidene-4'-*n*-propylaniline (HBPA), we have determined the sign of the axial electric field gradient ( $V_{zz}$ ) at the tin site in Sn-BBA.<sup>4,9,12</sup> Furthermore, an estimate of the quadrupole splitting ( $\Delta E_Q$ ) has been computed, and it is discussed in Sec. IV.

## II. EXPERIMENTAL

The details of the constant-acceleration Mössbauer spectrometer have been presented elsewhere.<sup>4</sup> The Mössbauer spectrum from Sn-BBA (5.2–5.68 wt %), Sn-PBPD (3.52 wt %), and Sn-TB (3.68 wt %) in BBOA was in each case fitted with a single Lorentzian line shape using a Burroughs 5500 computer. Since the linewidths for the samples were independent of  $\theta$ , the percent effect obtained from the computer fits was used as a measure of  $f$ . The 5- and 8-mCi sources of Sn-119 as BaSnO<sub>3</sub> used in these experiments were purchased from New England Nuclear Corporation. The alignment

procedure has been published previously.<sup>4</sup> Briefly, it consisted of cooling the system from the isotropic phase through the nematic, smectic *A*, and smectic *B* phases to room temperature in the presence of a 9000-G magnetic field. The disk-shaped sample (~1 cm in diam by ~2 mm thick) was then removed from the field and quickly frozen to 77°K in the Mössbauer absorber cryostat. The  $\gamma$  beam was always directed normal to the disk face. This procedure was repeated for each measurement.

The BBOA was prepared using standard techniques and recrystallized several times.<sup>13</sup> The tin-bearing solutes were dissolved into the BBOA by heating weighed amounts of the compounds to the isotropic phase for 2–3 h. The resulting solutions were checked via a polarizing microscope and by differential thermal analysis. Although the smectic *A*-nematic and the nematic-isotropic transitions were broadened and somewhat reduced in temperature, the integrity of each of the liquid-crystalline phases was maintained.

A typical Mössbauer spectrum is presented in Fig. 1. Table I lists the measured linewidths for each absorber molecule. The listed values correspond to averages for all the measurements on each compound. The minimum number of measurements at each  $\theta$  was seven for Sn-BBA, two for Sn-PBPD, and three for Sn-TB. Typically,

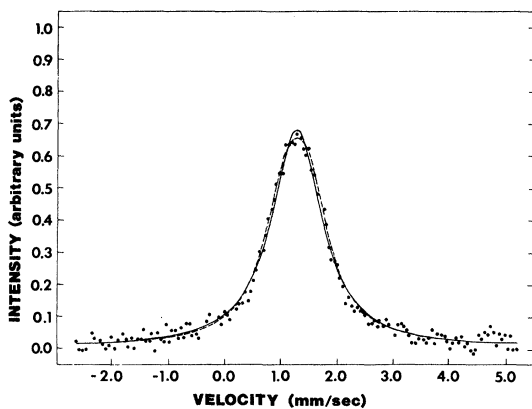


FIG. 1. Mössbauer spectrum observed for the absorber, 5.68% (by weight) of Sn-BBA in BBOA, aligned by a 9000-G magnetic field in the  $\theta=90^\circ$  orientation. The source was 5 mCi of Sn-119 as  $\text{BaSnO}_3$ . The solid line is a best fit of a single Lorentzian line shape to the data points. The dashed line is a composite line synthesized from two Lorentzian lines subject to the following constraints: (1) half-width at half-maximum for each line is 0.47 mm/sec, (2)  $(A_\pi/A_\sigma)=0.92$  as per Eq. (3), with  $S=0.17$ , and (3) the  $\sigma$  transition is at a higher velocity than the  $\pi$  transition. The two-line representation of the data is discussed in Sec. IV.

the number of measurements at  $\theta=0^\circ$  and  $\theta=90^\circ$  were double the above numbers.

### III. RECOIL-FREE FRACTION

For Sn-bearing solute molecules in liquid-crystalline glasses, the intramolecular and intermolecular vibrations may be considered to be uncoupled as is usually done for molecular crystals.<sup>10</sup> When these vibrations are not coupled, the recoil-free fraction can be approximated by a product of the intramolecular and intermolecular (lattice) contributions, and for a given molecule it is given by

$$f(\gamma, \rho) = f_M(\gamma)f_L(\rho) \propto \exp(-\epsilon_M \cos^2 \gamma) \exp(-\epsilon_L \cos^2 \rho), \quad (1)$$

where  $\gamma$  is the angle between the long molecular axis and the  $\gamma$ -ray direction, and  $\rho$  is the angle between the normal to the smectic layer (in which the molecule resides) and the  $\gamma$ -beam direction;  $\epsilon_M = (1/\lambda^2)(\langle x_{\parallel}^2 \rangle_M - \langle x_{\perp}^2 \rangle_M)$  is the molecular contribution to the nuclear vibrational anisotropy of the Sn atom and  $\epsilon_L = (1/\lambda^2)(\langle x_{\parallel}^2 \rangle_L - \langle x_{\perp}^2 \rangle_L)$  represents the lattice contribution to the Sn vibrational anisotropy; in  $\epsilon_m$  the  $\parallel$  and  $\perp$  mean square vibrational amplitudes  $(\langle x^2 \rangle_M)$  are with respect to the long molecular axis and in  $\epsilon_L$  the  $\parallel$  and  $\perp$  amplitudes  $(\langle x^2 \rangle_L)$  are with respect to the planar normal;  $\lambda$  is the reduced wavelength of the Mössbauer  $\gamma$  ray. In order to calculate the  $\theta$  dependence of  $f$  it is necessary to average Eq. (1) over the polar and azimuthal angles of both the molecule and the planar normal in the laboratory coordinate system.<sup>4</sup> The particular average over the polar angle ( $\delta$ ) of the molecular long axis must be weighted by the distribution function of Maier and Saupe,<sup>14</sup> namely,  $\exp[-(q/kT)\sin^2 \delta]$ , where  $q$  is the interaction energy,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. For triethyl-tin palmitate (Sn-Palm)  $[(C_2H_5)_3\text{SnOCOC}_{15}\text{H}_{31}]$  in the smectic *H* glass of HBPA both  $\epsilon_M (= -0.8)$  and  $q/kT (= 1.15)$  were determined from the  $\theta$  dependence of the quadrupole split area ratio  $(A_\pi/A_\sigma)$ .<sup>4</sup> Subsequent application of these values for  $\epsilon_M$  and  $q/kT$  to the  $\theta$  dependence of  $f$  resulted in a reduction in  $f(\theta)/f(\theta=0)$  (i.e., normalized to the  $\theta=0^\circ$  value) from 1.0 to only 0.87 as  $\theta$  in-

TABLE I. Linewidths (half-width at half-maximum) for each of the solutes in BBOA.

Solute	Linewidth (mm/sec)	Measurements
Sn-BBA	$0.55 \pm 0.02$	74
Sn-PBPD	$0.48 \pm 0.02$	21
Sn-TB	$0.49 \pm 0.02$	39

creased from  $0^\circ$  to  $90^\circ$ . This reduction in  $f$  accounted for only about 50% of its full  $\theta$  dependence. The remainder was due to the layered structure of the smectic  $H$  glass of HBPA. Since  $q/kT$  and the related order parameter ( $S$ ) of Maier and Saupe<sup>14</sup> are expected to be of approximately the same order of magnitude for Sn-Palm in HBPA and both Sn-BBA and Sn-PBPD in BBOA (see Sec. IV), the full  $\theta$  dependence of  $f$  for Sn-BBA and Sn-PBPD will not be accounted for by  $\epsilon_M$  (see Fig. 2).

The local distorted tetrahedral symmetry of the Sn atom in Sn-Palm is caused by the difference between the Sn-O bond and the three Sn-C bonds (to the ethyl groups). In Sn-BBA (and Sn-PBPD) the local symmetry is also that of a distorted tetrahedron because of the difference between the Sn-C bond to the carbon atom of the phenyl group (of the three member carbon chain) and the three Sn-C bonds to the methyl group carbon atoms. To properly consider the intramolecular contributions to the Sn-atom vibrational asymmetry in these molecules, all of the intramolecular normal-mode vibrations should be accounted for. Due to the extreme complexity of their molecular structure, such a calculation would be difficult; however, if one looks at the differences between the Sn-C bond and the Sn-O bond, a reasonable statement about relative anisotropies can be made. In particular, the Sn-C dissociation energies are not very sensitive to the organic group attached to the Sn-atom; however, they are quite different from the Sn-O dissociation energy in esters such as  $(C_2H_5)_3SnOCO(C_6H_5)$ ,<sup>15</sup> which is very similar to the Sn-Palm structure, with the only difference being a substitution of  $C_{15}H_{31}$  for the phenyl group. Furthermore, the bond length and force constant for the Sn-C bond are not very dependent on the organic group attached to the Sn atom, but they are distinctly different from their counterparts in the Sn-O bond.<sup>16</sup> Consequently, one expects the magnitude of  $\epsilon_M$  for both Sn-BBA and Sn-PBPD to be much less than the Sn-Palm value of  $\epsilon_M = |0.8|$ . As a result, the lattice contribution to the Sn vibrational anisotropy will almost totally account for the  $\theta$  dependence of  $f$  [as  $f(\theta)/f(\theta=0)$ ] for both Sn-BBA and Sn-PBPD in BBOA. The differences in the  $\theta$  dependence of  $f$  for Sn-BBA, Sn-PBPD, and Sn-TB ( $\epsilon_M = 0$  for this molecule) are accounted for below by considering the differences in their shapes relative to the shape of the host BBOA molecules of the layered smectic  $B$  glass.

In considering the lattice contribution to the  $\theta$ -dependence of  $f$ , the smectic  $B$  glass of BBOA provides a much simpler system than the previously used smectic  $H$  glass phase of HBPA,<sup>4,9</sup>

because the tilt of the preferred molecular direction from the planar normal and the interplanar translational order of the smectic  $H$  structure<sup>17</sup> are both absent in the smectic  $B$  phase of BBOA. The characteristic tilt angle of HBPA had not been measured by a technique other than the Mössbauer effect, and, as a result, both the tilt angle ( $\tau$ ) and the lattice contribution to the vibrational anisotropy ( $\epsilon_L$ ) had to be extracted from the  $f$ -vs- $\theta$  data.<sup>9,12</sup> Here, in the smectic  $B$ , since  $\tau = 0^\circ$ , only  $\epsilon_L$  appears in the expression for  $f(\theta)$  (normalized to the  $\theta = 0^\circ$  value) as follows:<sup>4,8,9</sup>

$$f(\theta)/f(\theta=0) = e^{-\epsilon_L \sin^2 \theta} + C, \quad (2)$$

where  $\epsilon_L$  has been defined above. The constant  $C$ , which has been added to the right-hand side of Eq. (2), allows the theoretical curve to be raised or lowered without distorting its shape and has the effect of not forcing the theory and experiment to coincide at  $\theta = 0^\circ$ .

The data for all three solutes in BBOA are presented in Fig. 2. The curves are the best fits of Eq. (2) to the data. They were made using a Burroughs 5500 computer. The resulting best-fit parameters are listed in Table II.

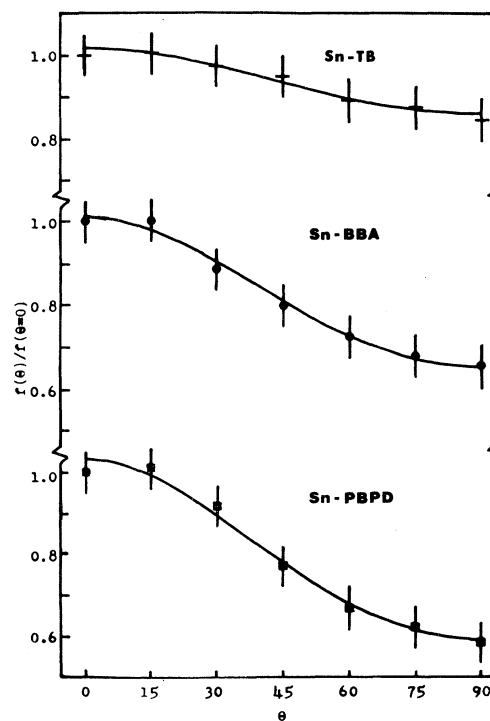


FIG. 2. Plot of the  $f(\theta)/f(\theta=0)$ -vs- $\theta$  data for Sn-BBA (●), Sn-PBPD (■), and Sn-TB (+) in BBOA. The Mössbauer absorbers were at 77 °K. The solid lines are best fits of the theory [see Eq. (2)] to the experimental data points.

Clearly, the range of values of  $\epsilon_L$  listed in Table II emphasizes that the three solutes are not sampling the same vibrational properties of the liquid-crystalline glass. The data for Sn-BBA and Sn-PBPD are similar to the Mössbauer studies of these molecules in a smectic *H* liquid-crystalline glass (namely, HBPA at 77°K).<sup>9</sup> That is, the longer molecule exhibits a larger negative value of  $\epsilon_L$ , which is probably due to the fact that it (Sn-PBPD) is likely to penetrate a second layer, since it is roughly the same length as the BBOA (32 Å) and larger than the HBPA (28 Å) molecules. Thus, in a manner similar to the HBPA case, in BBOA one would expect a smaller value for  $\langle x_{\parallel}^2 \rangle_L$  for the Sn-PBPD; given that  $\langle x_{\perp}^2 \rangle_L$  is roughly the same for both Sn-BBA and Sn-PBPD. (This latter assumption is probably pretty good, because both molecules are nearly the same width as the BBOA, with benzene rings near the molecular center.) This follows because of the steric problems encountered by a molecule whose length is greater than the thickness of the smectic layer.

Interestingly, the  $\epsilon_L$  values measured in BBOA are larger negative numbers than the  $\epsilon_L$  values measured in HBPA for the identical solutes (-0.45 vs -0.39 for Sn-BBA and -0.58 vs -0.55 for Sn-PBPD).<sup>9,12</sup> This agrees with the fact that the smectic *H* phase possesses more three-dimensional order and less mobility anisotropy than the smectic *B* phase.<sup>3,17</sup> For example, the anisotropy of diffusion, would be expected to be greater for the smectic *B* than for the smectic *H*. Therefore, the result that the anisotropy of the molecular vibrational amplitudes is greater in the smectic *B* glass than in the smectic *H* glass is not unexpected.

As shown in Fig. 2 and Table II the  $\theta$  dependence of  $f$  and the resulting negative value for  $\epsilon_L$  from the Sn-TB measurement are distinctly less than for the other solutes. To explain these differences we first look at the molecular shapes of the solutes. The Sn-TB is nearly spherical, as opposed to the long, rather flat, shapes of Sn-BBA, Sn-PBPD, and BBOA, itself. Furthermore, its diameter is nearly double the width of the other molecules, and, no doubt, influences the positioning of this solute in the BBOA. There must necessarily be distortion of the molecular packing in the vicinity of the Sn-TB molecule. Murphy and Doane have made NMR studies of diffusion in smectic liquid crystals using the spherical molecule, tetramethylsilane (TMS).<sup>18,19</sup> These studies indicate that the TMS molecule resides in the more fluid regions made up of the flexible alkyl end chains rather than in the regions made up of the relatively inflexible central portions of the liquid-crystalline host molecules. In addition, it is known that

the end chains are less ordered than the central cores of the liquid-crystal molecules and thus less characteristic of the layer anisotropy.<sup>20-22</sup> Therefore, if in the nematic and smectic phases the Sn-TB molecules are in the more fluid regions of the alkyl end chains, then this end-chain region will also be their likely locale in the smectic *B* glass. The lower value of  $\epsilon_L$  obtained in the Sn-TB experiments is in accord with the above. That is, because the smaller, more spherical Sn-TB molecule experiences less of the layer anisotropy than the longer solutes and the host BBOA molecules (see Fig. 2), it most likely resides in the region of the flexible end chains of the BBOA molecules. In fact, this points out that the segments of the host liquid-crystalline molecules are individually important in determining the vibrational motion in the glassy state. The Mössbauer results on the frozen glass are therefore consistent with the known properties of the normal (nonglassy) smectic phases.

#### IV. LINE POSITION

The apparent line position of the Sn-119 Mössbauer absorption for Sn-BBA in BBOA increased from  $1.234 \pm 0.020$  mm/sec to  $1.298 \pm 0.020$  mm/sec (with respect to the  $\text{BaSnO}_3$  source) as  $\theta$  increased from  $0^\circ$  to  $90^\circ$ . In contrast, the line positions for the solutes Sn-PBPD ( $1.27 \pm 0.02$  mm/sec) and Sn-TB ( $1.38 \pm 0.02$  mm/sec) in BBOA displayed no  $\theta$  dependence. Interestingly, of the three solutes, Sn-BBA, Sn-PBPD, and Sn-Palm, used in the smectic *H* glass of HBPA, only the line position of Sn-BBA exhibited a  $\theta$  dependence. In fact, for Sn-BBA, the scatter of the data points and their angular variation in the smectic *H* glass were comparable to results in the smectic *B* glass.<sup>23</sup> The quantity of reproducible data for the different solutes rules out any systematic errors in our experimental system. That is, if there were any systematic errors, each solute would have exhibited a  $\theta$ -dependent line position.

The linewidth for each solute was found to be independent of  $\theta$ . Table I lists the average values of the half-width at half-maximum for each solute. These half-widths were obtained from the best

TABLE II. Values of  $\epsilon_L$  and  $C$  resulting from the best fit of Eq. (1) to the  $f(\theta)/f(\theta=0)$ -vs- $\theta$  data in BBOA.

Solute	$\epsilon_L$	$C$
Sn-BBA (length, 18 Å)	-0.45	0.010
Sn-PBPD (length, 32 Å)	-0.58	0.030
Sn-TB (diam, 12 Å)	-0.17	0.015

fit of a single Lorentzian lineshape to each spectrum (see Fig. 1). From Table I, however, the average linewidth for the Sn-BBA solute is seen to be 12–13% greater than for either Sn-PBPD or Sn-TB and more than 50% greater than the uncertainty principle minimum.<sup>24</sup> When this is coupled with the fact that the entire shift in line position (i.e., from  $\theta = 0^\circ$  to  $\theta = 90^\circ$ ) for the Sn-BBA is only 0.064 mm/sec and, therefore, only 6% of the full linewidth, the existence of an unresolved quadrupole doublet becomes a reasonable possibility.

For the case of an unresolved quadrupole doublet, the separate  $\theta$  dependence of each transition causes a shift in the apparent line position. The area ratio ( $A_\pi/A_\sigma$ ) for the  $\pi$  and  $\sigma$  transitions in a  $I = \frac{3}{2} - I = \frac{1}{2}$  system has been computed.<sup>4,25</sup> For the particular case, in which the molecular contribution to the nuclear vibrational anisotropy ( $\epsilon_M$ ) is zero or very close to zero, the result is

$$\frac{A_\pi}{A_\sigma} = \frac{1 + \frac{1}{4}(3 \cos^2 \theta - 1) \langle \frac{1}{2}(3 \cos^2 \delta - 1) \rangle}{1 - \frac{1}{4}(3 \cos^2 \theta - 1) \langle \frac{1}{2}(3 \cos^2 \delta - 1) \rangle}. \quad (3)$$

Here  $\theta$  is the experimental angle between the preferred molecular direction and the  $\gamma$  beam and  $\delta$  is the angle between the molecular long axis of a particular molecule and the preferred direction. The quantity  $\langle \frac{1}{2}(3 \cos^2 \delta - 1) \rangle$  is designated as  $S$  and defined as

$$S = \frac{\int_0^\pi \frac{1}{2}(3 \cos^2 \delta - 1) \exp[-(q/kT) \sin^2 \delta] \sin \delta d\delta}{\int_0^\pi \exp[-(q/kT) \sin^2 \delta] \sin \delta d\delta}. \quad (4)$$

Here,  $S$  is called the order parameter of Maier and Saupe.<sup>14</sup> Note that if the solute molecules are not ordered by the liquid-crystalline host, then  $S = 0$  and ( $A_\pi/A_\sigma$ ) is independent of  $\theta$  and the apparent line position of an unresolved doublet will also be independent of  $\theta$ .

In an electron spin resonance investigation of the solute order parameter of several vanadyl complexes in the nematic phase of *p*-azoxyanisole, Glarum and Marshall demonstrated that the solute  $S$  value increased as the solute length increased.<sup>26</sup> The same kind of phenomena has been demonstrated by the Mössbauer observations of solutes in a liquid-crystalline glass. In particular, the  $\theta$  dependence of ( $A_\pi/A_\sigma$ ) has been observed both for the Fe-57 quadrupole split spectrum of 1, 1'-diacetylferrocene (DAF) and the Sn-119 quadrupole split spectrum of Sn-Palm in the smectic *H* glass of HBPA. The rather short DAF molecules ( $\sim 7 \text{ \AA}$ ) exhibited a  $\theta$ -independent area ratio ( $A_\pi/A_\sigma$ ) near unity and therefore were not ordered ( $S = 0$ ) by the liquid-crystalline host.<sup>27</sup> In contrast, the Sn-Palm molecules which have ex-

tended molecular lengths of 26  $\text{\AA}$  displayed a marked  $\theta$ -dependent area ratio. From these data  $S$  was determined to be  $S = 0.17$  for Sn-Palm in HBPA at 77°K.<sup>4</sup> The magnitude of  $S$  and its calculation for Sn-Palm in HBPA have been discussed at length in Ref. 4.

A comparison of extended molecular lengths shows that Sn-Palm and HBPA are 26 and 28  $\text{\AA}$ , respectively, and that Sn-BBA and BBOA are 18 and 32  $\text{\AA}$ , respectively. We see that the length ratio of Sn-BBA to BBOA is therefore only 60% of the length ratio of Sn-Palm to HBPA. Consequently, on the basis of molecular lengths alone one would expect that the  $S$  value for Sn-BBA in BBOA would be smaller than the  $S$  value of Sn-Palm in HBPA. The Sn-Palm molecule, however, is more flexible than the Sn-BBA molecule because it possesses a very long alkyl chain ( $C_{15}H_{31}$ ) and lacks the rigid core of the Sn-BBA molecule as shown in Fig. 3. This additional flexibility may allow the Sn-Palm to partially curl back on itself and cause its  $S$  value in HBPA to be smaller than the  $S$  value of a more rigid molecule of the same length. As a result, it is difficult to say whether  $S$  for the Sn-Palm in HBPA is larger or smaller than  $S$  for Sn-BBA in BBOA; however, one can reasonably expect that the respective  $S$  values are about the same order of magnitude and probably within a factor of 2 of one another. Of importance is the fact that the  $S$  value for both Sn-Palm and Sn-BBA in their respective host liquid crystals must be positive. That is, to be consistent with known liquid crystal data<sup>2,5,14,27</sup> the preferred molecular direction of solutes such as Sn-Palm and Sn-BBA must be parallel to the preferred molecular direction of the aligned liquid-crystalline host molecules. For the case described by Eq. (3) (and therefore, for Sn-BBA in BBOA) it is seen that when  $S$  is positive ( $A_\pi/A_\sigma > 1$  for  $\theta = 0^\circ$  and ( $A_\pi/A_\sigma < 1$  for  $\theta = 90^\circ$ ). Consequently, the  $\sigma$  transition must grow with respect to the  $\pi$  transition as  $\theta$  increases from  $0^\circ$  to  $90^\circ$ . Since the apparent line position of the Sn-BBA absorption shifts to more positive velocities as  $\theta$  increases, the  $\sigma$  transition must occur at a more positive velocity than the  $\pi$  transition. The expression for the quadrupole splitting for an axially symmetric electric field gradient ( $V_{zz}$ ) and

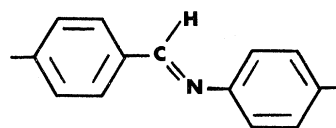


FIG. 3. Diagram of the rather rigid core of the Sn-BBA molecule.

a nuclear spin state of  $I = \frac{3}{2}$  is

$$\Delta E_Q = E_\pi - E_\sigma = eV_{zz}Q, \quad (5)$$

where  $Q$  is the quadrupole moment and  $e$  is the proton charge. As a result, the quantity  $eV_{zz}Q$  must be negative for the Sn-BBA molecule. Since  $Q$  is known to be negative for the  $I = \frac{3}{2}$  state of Sn-119,<sup>24</sup> the quantity  $V_{zz}$  must be positive for the Sn-BBA molecule.

The next step is to estimate the value of  $\Delta E_Q$  for the Sn-BBA molecule. To do this we made the rough estimate that  $S \approx 0.17$  and then reconstructed the data subject to the following conditions: (i) the apparent single line absorption is a Lorentzian line shape with half-width at half-maximum of 0.55 mm/sec (see Table I); (ii) the half-width at half-maximum for each member of the unresolved doublet is 0.47 mm/sec (from Table I this is the approximate singlet linewidth); (iii) the line position of the apparent single line for  $\theta = 90^\circ$  is +0.064 mm/sec with respect to the  $\theta = 0^\circ$  line position; (iv) the intensity for  $\theta = 90^\circ$  is 0.65 of the intensity for  $\theta = 0^\circ$  (see Fig. 2); and (v)  $(A_\pi/A_\sigma) = 1.19$  for  $\theta = 0^\circ$  and  $(A_\pi/A_\sigma) = 0.92$  for  $\theta = 90^\circ$  as per Eq. (2), with  $S = 0.17$ . The resulting synthesis of the apparent single line absorption yielded adequate representations of the experimental data (see Fig. 1) and  $\Delta E_Q \approx 0.4$ . Because of the uncertainty in the  $S$  value for Sn-BBA in BBOA the error in this value for  $\Delta E_Q$  may be as high as  $\pm 0.2$  mm/sec.

#### V. THE UNORIENTED SAMPLE

The line position for the unoriented sample (i.e., the sample was cooled in zero magnetic field) of Sn-BBA in the smectic  $B$  glass is very near the  $\theta = 90^\circ$  value. This is in agreement with the  $f$  data for all three solutes in the unoriented smectic  $B$  glass. Table III shows that the value of the line position for Sn-BBA and the normalized values of  $f$  for all three solutes in the unaligned host are very close to the values for the  $\theta = 90^\circ$  orientation. This shows that the molecular alignment induced by the surfaces of the disk-shaped sample is for the most part parallel to the disk face. We suggest that competition from the rim explains the slightly higher values of  $f$  and the

TABLE III. Data for the smectic  $B$  glass of BBOA at 77 °K. A comparison of data from unoriented samples (i.e., cooled in zero magnetic field) with data from samples oriented at  $\theta = 90^\circ$ .

Solute	$f/f(\theta=0)$		Line position (mm/sec)	
	$\theta = 90^\circ$	Unoriented	$\theta = 90^\circ$	Unoriented
Sn-BBA	0.65	0.77	1.298	1.279
Sn-PBPD	0.58	0.68		
Sn-TB	0.85	0.89		

lower velocity line position for the unoriented samples. The result that the surface alignment corresponds to  $\theta = 90^\circ$  is in agreement with the results of the  $A_\pi/A_\sigma$  and  $f$  data for Sn-Palm in HBPA and the  $f$  data for Sn-BBA and Sn-PBPD in HBPA.<sup>4,23</sup>

#### VI. CONCLUSION

The vibrational anisotropy of the smectic  $B$  glass (at 77°K) has been observed using the orientational dependence of the recoil-free fraction of Sn-bearing solutes in BBOA. The anisotropy of the mean-square vibrational amplitudes can be understood via the differences in the central core and end-chain regions of the host BBOA molecules. In addition, a new way of obtaining molecular information from an unresolved quadrupole doublet has been found. In particular, the sign of  $V_{zz}$  has been determined to be positive and the magnitude of the quadrupole splitting found to be  $\Delta E_Q = 0.4$  mm/sec for tin in the Sn-BBA molecule. In experiments in which a large Zeeman field ( $> 40\,000$  G) is used to distinguish the  $\pi$  transition from the  $\sigma$  transition, the sign of  $V_{zz}$  is inaccessible unless the quadrupole splitting is well resolved.<sup>28</sup> Therefore, the use of liquid-crystalline solvents may be very helpful in determining molecular information for molecules known to exhibit an unresolved quadrupole splitting.

#### ACKNOWLEDGMENT

One of us (D.L.U.) would like to thank Dr. V. D. Neff for helpful discussions concerning atomic and molecular vibrations.

\*This work was supported in part by the National Science Foundation, under Grant Nos. GH34164X and DMR7413173.

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