

*Liquid
Crystals and
Ordered
Fluids*

3

Edited by J. F. Johnson and R. S. Porter

Liquid Crystals and Ordered Fluids

Volume 3

Edited by

JULIAN F. JOHNSON

*Institute of Materials Science
University of Connecticut
Storrs, Connecticut*

and

ROGER S. PORTER

*Materials Research Laboratory
Department of Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts*

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Liquid Crystals and Ordered Fluids

Volume 3

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*Volume 1 – Proceedings of an American Chemical Society Symposium,
New York City, September, 1969*

*Volume 2 – Selected papers from a symposium of the Division of Colloid
and Surface Chemistry, Chicago, August, 1973*

*Volume 3 – Selected papers from a symposium of the Division of Colloid
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PREFACE

This volume represents a collection of selected papers from a symposium of the Division of Colloid and Surface Chemistry held during the national meeting of the American Chemical Society in Chicago, August 1977.

A variety of experimental techniques has been used in these studies including dynamic calorimetry, equilibrium calorimetry, Raman spectroscopy, NMR, depolarized fluorescence, acoustical/optical effects, EPR, and photochemical methods. The range of systems studied is similarly broad, including both lyotropic and thermotropic materials ranging from biological systems through synthetic organic liquid crystals.

The variety of study modes ranges from applied studies to highly theoretical treatments.

Historically, the amount of research in the area of liquid crystals has fluctuated widely, with peaks of activity around 1900 and in the 1930's. For the period that began in 1960 liquid crystal research appears to have peaked and has now settled down to be a stable field with many investigators involved but lacking both the periods of rapid acceleration and deceleration of effort that characterized it earlier.

Julian F. Johnson
Institute of Materials Science
University of Connecticut
Storrs, Conn. 06268

Roger S. Porter
Polymer Science & Engineering
University of Massachusetts
Amherst, Mass. 01002

CONTENTS

Raman Spectroscopic and Calorimetric Investigation of the Multiple Smectic Phase Material TBBA	1
J. M. Schnur and J. P. Sheridan	
Thermal Properties of a New Series of Liquid Crystals Forming Materials: p,p'-DI-n-Alkyldiphenyl and p,p'- DI-n-Alkoxydiphenyldiacetylenes	19
E. M. Barrall, II, Barbara Grant, Annie R. Gregges	
The Preparation and Thermodynamic Properties of Some Chiral 4-Alkyl-4'-Cyanostilbenes and Tolans	41
Robert J. Cox, Nicholas J. Clecak, and Julian F. Johnson	
A Simple and Inexpensive Synthetic Method for Alkylcyanobiphenyls	53
Chan S. Oh	
Effect of Molecular Structure on Mesomorphism. 6. Non-linear Thermal Behavior in Some Binary Liquid Crystal Systems	61
Anselm C. Griffin, Thomas R. Britt, Neal W. Buckley, Richard F. Fisher, Stephen J. Havens, and D. Wayne Goodman	
Liquid Crystalline Interactions Between Cholesteryl Esters and Phospholipids	75
Martin J. Janiak and Carson R. Loomis	
Polymers of β -Lactam Antibiotics: Structural, Chemical and Biological Properties	89
M. K. Stanfield, B. L. Warren, and F. H. Wilson	

Magnetic Relaxation of Small Molecules in Ordered Fluids and Liquid Crystals	107
B. M. Fung, John H. Johnson, and E. A. Grula	
Absorbance and Pitch Relationships in Dichroic Guest-host Liquid Crystal Systems	117
H. S. Cole, Jr. and S. Aftergut	
The Self Control of Lipid Bilayers	133
Donald L. Melchior and Joseph M. Steim	
Transitions Within the Cholesteric Mesophase of Cholesteryl Stearate	151
Lidia Roche Farmer and Paul F. Waters	
Domains Due to Electric and Magnetic Fields in Bulk Samples of Liquid Crystals	165
E. F. Carr	
The Determination of Moments of the Orientational Distribution Function in Liquid Crystals by the Depolarization of Fluorescence of Probe Molecules	177
L. Lawrence Chapoy, Donald B. DuPré, and Edward T. Samulski	
Lateral Species Separation in the Lipid Bilayer	191
P. H. Von Dreele	
Formation of the Liquid Crystals of Polyribonucleotide Complexes	197
Eisaku Iizuka and Jen Tsi Yang	
Theoretical Model for the Phospholipid Bilayer System: Single Component Phase Transition and Binary Mixture Phase Diagram	209
R. G. Priest and J. P. Sheridan	
The Ordering of Cholesteric Mesophases by Linear Cellulosic Polymers	225
T. Sarada and P. F. Waters	
Effect of Liquid Crystalline Material on Stability of Nonaqueous Foam	243
Syed Iftikhar Ahmad	
Spectroscopic Studies of Dyes in Liquid Crystal Impregnated Microporous Polypropylene Films	259
E. J. Poziomek, T. J. Novak, and R. A. Mackay	

Thermal and Chemical Perturbations of Molecular Order at the Interface and in the Alkyl Chain Region of a Lyotropic Liquid Crystal	271
Robert C. Long, Jr. and J. H. Goldstein	
The Acousto-Optic Effect for a Nematic Liquid Crystal in the Presence of an Applied Electric Field	287
C. F. Hayes	
Microcontinuum Theory of Heat-conducting Smectic Liquid Crystals	297
M. N. L. Narasimhan and T. E. Kelley	
Orientational Effects in Heat-conducting Smectic Liquid Crystals	319
M. N. L. Narasimhan and T. E. Kelley	
Fluctuations and Ordering in Nematic Liquid Crystals	347
Roger Chang	
Correlation Function Approach to the Study of Raman Band Shapes of Liquid Crystals	355
Kenneth Brezinsky and Bernard J. Bulkin	
Lattice Model Treatments of the Formation of Ordered Phases in Stiff Chain Polymer-Diluent Systems	371
Elizabeth L. Wee and Wilmer G. Miller	
A Lattice of Rigid Rods with Long Range Anisotropic Attractions	385
Michael S. Rapport and Andrew G. De Rocco	
An EPR Investigation of a Nematogen-like Nitroxide Spin Probe in the Solid Modifications of a Liquid Crystal	399
Arthur E. Stillman, Loretta L. Jones, Robert N. Schwartz, and Barney L. Bales	
Conduction Currents Associated with the Variable Grating Modes in Nematic Liquid Crystals	421
P. K. Watson, J. M. Pollack, and J. B. Flannery	
Micropolar Theory of Liquid Crystals	443
A. Cemal Eringen	

Photochemical and Thermal Stability Studies on a Liquid Crystal Mixture of Cyanobiphenyls	475
Frederick G. Yamagishi, Deborah S. Smythe, Leroy J. Miller, and J. David Margerum	
A New Method for Inducing Homogeneous Alignment of Nematic Liquid Crystals	497
Michael J. Little, Hugh L. Garvin, and Leroy J. Miller	
A New Method for Inducing Homeotropic and Tilted Alignments of Nematic Liquid Crystals on Silica Surfaces	513
Leroy J. Miller, Jan Grinberg, Gary D. Myer, Deborah S. Smythe, and Willis H. Smith	
Index	531

RAMAN SPECTROSCOPIC AND CALORIMETRIC INVESTIGATION OF THE MULTIPLE
SMECTIC PHASE MATERIAL TBBA

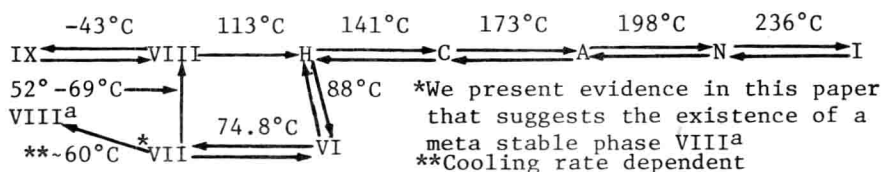
J. M. Schnur and J. P. Sheridan

Naval Research Laboratory

Washington, D. C. 20375

INTRODUCTION

Smectic mesophase formation and structure have been the subject of vigorous scientific inquiry in recent years.¹⁻⁶ Among those phases investigated most intensively, the B and H phases are thought to possess the highest degree of local three-dimensional order. As determined by X-ray crystallography¹⁻⁵ both phases exhibit long-range two dimensional pseudo-hexagonal order within each layer; in addition there appears to be some degree of correlation between planes.^{1,5} In the H phase the director lies at an angle to the smectic planes, while in the B phase it is normal to the planes. The nature of the degrees of freedom available and the intermolecular ordering in these phases has been the subject of a number of theoretical and experimental studies.^{3,7,8} Since terephthal-bis-butylaniline (TBBA) exhibits a smectic H phase as well as at least eight other phases (see schematic below), it has been extensively studied by various experimental techniques including X-ray,⁴ NMR,⁹ DSC,¹⁰ neutron scattering,¹¹ infrared¹² and Raman^{10,13-14} spectroscopy. This paper provides new information on the nature of the various smectic phases observed in TBBA. We present new spectroscopic and thermodynamic data about TBBA, and two of its deuterated isotopes, obtained in its various solid and smectic phases. Both the Raman and calorimetric techniques have provided new insights into the nature of these smectic phases and the mechanisms of the transition.



Changes in the Raman spectra have been observed between a number of the phases, the most dramatic differences being seen between the solid and H phases. Specifically, there is clear evidence that substantial "melting" of the butyl hydrocarbon end-groups occurs upon entering the H phase. There are also changes in other spectral regions which suggest that one or two of the aromatic rings begin to rotate with respect to each other in the H phase. These points are consistent with the NMR,⁹ and neutron scattering¹¹ studies which support the model of the alkyl end groups being fairly mobile and liquid-like in the H-phase, and the possible existence of a correlated motion of the molecules around their long axes, which also can explain the pseudo-hexagonal symmetry observed in the X-ray¹ experiments. Furthermore, the Raman data suggest that phase VI lies intermediate in structure between the smectic H phase and the solid phase VIII while phase VII is very similar on a local scale to the molecular structure of phase VIII.

In addition, while the spectroscopic data obtained upon heating a virgin crystal compared quite well with previously published results,¹³ it was found that recycling the samples produced unusual and, at first, not easily reproducible results.

Specifically, a sharp low frequency band ($\sim 20\text{ cm}^{-1}$) appeared in some cases but not in others, and the solid-smectic H phase transition temperature appeared to vary. Consequently a comprehensive DSC study of the effects of thermal history on TBBA was initiated. This study demonstrated that there are three solid phases, one that exists below -43°C , the other two existing above that temperature. One of these phases may be metastable with respect to the other or the effect may be a kinetic one. As a result of this study, we have learned how to control the sample history so as to yield consistent reproducible results. Recently, Raman spectra have been published¹⁴ which did not seem to agree with our previously reported results.¹³ By appropriately varying sample history and quenching we can now reproduce both Dvorjetski's¹⁴ work and our earlier spectra.

EXPERIMENTAL

Raman

The experimental arrangement consisted of a Spex 14018 double monochromator with an RCA 31034 cooled photomultiplier tube and a photon counting system. The spectra were enhanced by the use of zero suppression and scale expansion techniques. The excitation source was a Coherent Krypton 500K laser providing 80 mW of 7525Å radiation at the sample. This near infrared line of the Krypton laser provided the best spectra, since it minimized both photo-degradation of the sample and background fluorescence. The samples were contained in 1 mm glass capillary tubes. The laser beam was focused upon the sample to approximately a 50 μ m diameter, and 90° scattering from the illuminated region was then sampled. Both the exciting and scattered radiation were scrambled to minimize the spurious birefringent contributions possible in anisotropic mesomorphic systems. The temperature was continuously monitored and was accurate to within $\pm 0.5^\circ\text{C}$; fluctuations were less than $\pm 0.2^\circ\text{C}$.

At higher temperatures the spectra were obtained by running several samples in different but overlapping spectral regions. TBBA and two of its isotopes were studied in all observed phases except the isotropic. The structures of these materials are described elsewhere.¹⁰ It was found that the material with the deuterated centers (TBBA-DC) was of highest initial purity, and consequently provided the best spectra at highest temperatures. TBBA and TBBA deuterated tails (TBBA-DT) were obtained as a gift from Jean Charvolin, Laboratoire des Solides, Universite de Paris, Orsay, France and TBBA-DC was a gift from Sol. Meiboom, Bell Laboratories, Murray Hill, New Jersey.

Calorimetry

A Perkin-Elmer scanning microcalorimeter model #DSC-2 was used to obtain the calorimetric data. The machine was calibrated for use to 100°K. The samples were placed in hermetically sealed aluminum containers in a rigorously dry argon atmosphere. Scanning rates varied between 1.25°/mm and 5°/mm.

RESULTS

Spectroscopic

The most dramatic differences between the H and solid phase occur in the 300 cm^{-1} and 1500 cm^{-1} region. In order to attribute these changes to molecular conformations and motions, TBBA-DT (deuterated tail) and TBBA-DC (deuterated centers) were studied. Figure 1 shows the Raman spectra for TBBA, TBBA-DC, and TBBA-DT,

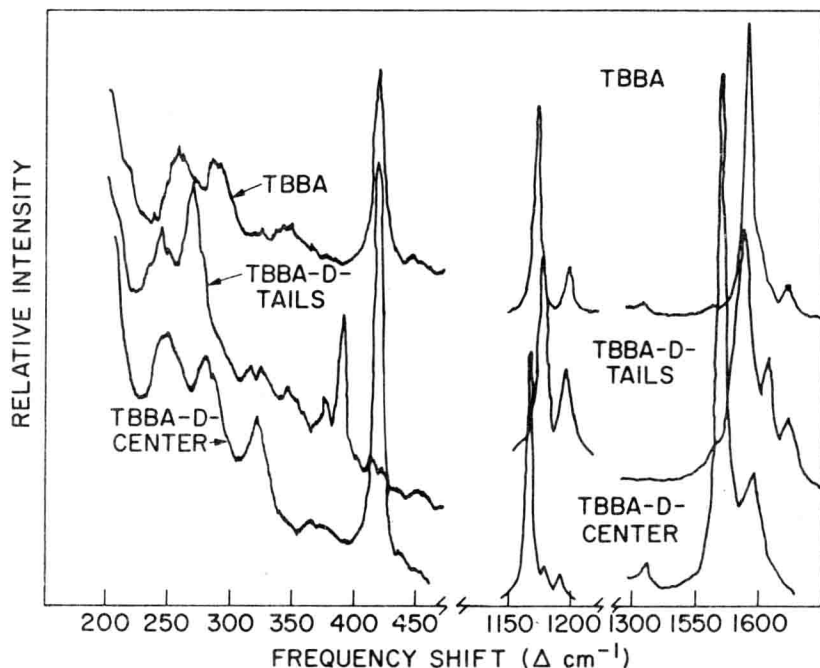


FIGURE 1 - Raman Spectra of TBBA, TBBA-DC, and TBBA-DT in the 200-450, 1150-1200, and 1500-1650 cm^{-1} regions. Spectral resolution is 3 cm^{-1} .

at 30°C for the 200 cm^{-1} -450 cm^{-1} , 1150 cm^{-1} -1200 cm^{-1} , 1500 cm^{-1} -1650 cm^{-1} regions. The deuteration of the tails has apparently reversed order of the peaks in the 250-300 cm^{-1} region, the smaller of the two appears to have shifted from ~285 cm^{-1} to ~245 cm^{-1} . The more intense band at ~418 cm^{-1} has also shifted slightly lower in frequency. The shift upon deuteration, the location of the non-deuterated band, coupled with the Raman studies of alkanes,¹⁸ alkylbenzenes,¹⁹ and alkoxy azoxybenzenes²⁰ strongly suggest that the 285 cm^{-1} band is associated with a group motion of the butyl side groups, most probably the all trans accordion band.

Previous work on Schiff bases²¹ has indicated that the bands

in the 1550 cm^{-1} - 1650 cm^{-1} region are associated with the $\text{R}-\overset{\text{H}}{\text{C}}=\text{N}$ linkage. Upon deuteration of the centers TBBA-DC - the bands observed in this region (both solid and H phase) shift downward approximately 30 cm^{-1} thus confirming that these bands provide information on the central portion of the TBBA molecule.

Raman spectra for TBBA solid and H phases in the 200 - 600 , 1100 - 1250 , and 1500 - 1700 cm^{-1} region are shown in Figure 2. The most dramatic spectral change is observed in the 1500 - 1700 cm^{-1} region. In the solid phase only a trace of a band exists at about 1560 cm^{-1} . Upon entering the H phase this band dramatically increases a factor of 40 when compared to the 1170 cm^{-1} band. The 1170 cm^{-1} band does not change appreciably as a function of temperature. Figure 3 shows a plot of the intensity of the 1560 cm^{-1} band relative to the 1170 cm^{-1} band as a function of temperature through the solid-smectic H phase transition region. There is no evidence of pretransition effects and the sharpness of the intensity change at the phase transition temperature is indicative of a highly cooperative event.

Another important set of spectral changes occur in the 280 - 350 cm^{-1} region. The band at 285 cm^{-1} in the solid phase decreases in a more or less sigmoidal fashion upon nearing and entering the smectic H phase. Simultaneously a group of bands at somewhat higher frequencies (310 - 350 cm^{-1}) begins to increase in intensity in the phase transition region and becomes quite dominant in the H phase. The temperature dependence of the relative intensities (compared to the 1170 cm^{-1} band) of the 285 cm^{-1} band and the envelope of bands at 310 - 350 cm^{-1} is shown in Fig. 4. As can be seen from the figure, the intensity changes are less sharp at the phase transition temperature than that displayed by the 1560 cm^{-1} band and there is evidence of some pretransition changes. However both curves display the sigmoidal behavior expected from a cooperative first-order phase change. Upon heating through the smectic phases C and A and on into the nematic phase only small increases in the relative intensities of the 310 - 350 cm^{-1} envelope occur accompanied by a slight decrease in intensity of the 285 cm^{-1} band. Similarly, there is little or no change in the relative intensity of the 1560 cm^{-1} as a function of phase upon heating.

However, upon cooling the sample, we observed some further interesting changes in these spectral regions. Figure 5(a) and (b) show the spectra obtained in the 200 - 450 cm^{-1} region for Phases VI and VII respectively. In Phase VI it appears that the 285 cm^{-1} has regained considerable intensity while some of the higher frequency bands (notably at $\sim 315\text{ cm}^{-1}$) persist. In Phase VIII most of the 310 - 350 cm^{-1} envelope has disappeared and the 285 cm^{-1} is even stronger. Furthermore, the strong quasi-elastic scatter

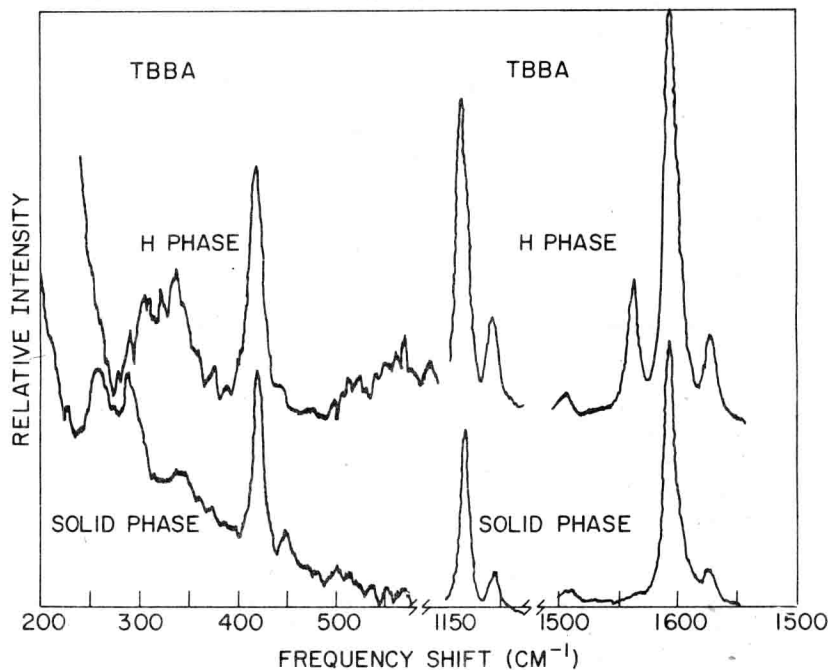


FIGURE 2 - Raman spectra of TBBA solid and H phase in the 200-600, 1100-1250, and 1500-1700 cm^{-1} region. Spectral resolution is 3 cm^{-1} .

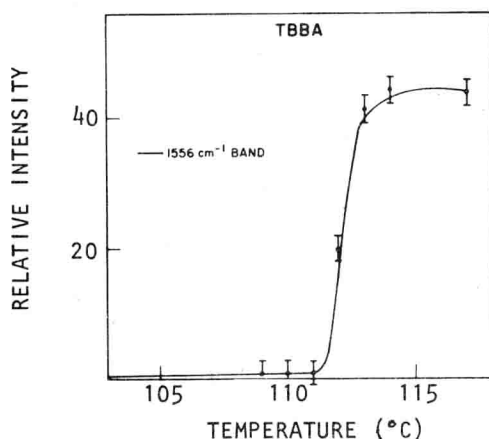


FIGURE 3 - Temperature dependence of the intensity of the 1560 cm^{-1} band relative to the 1170 cm^{-1} band through the solid-smectic H transition region.

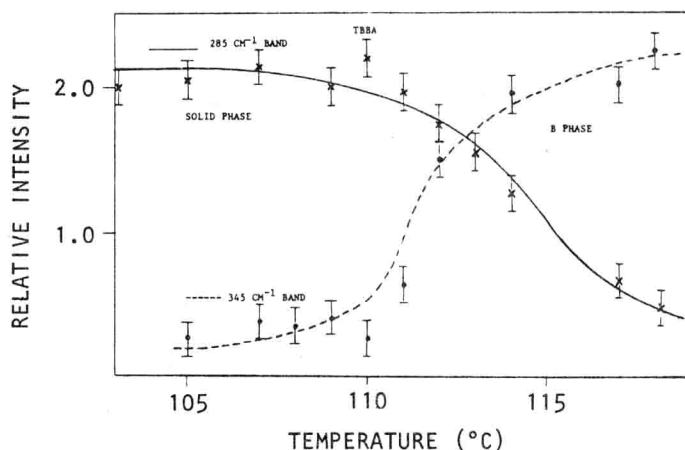


FIGURE 4 - The temperature dependence of the relative intensities (compared to the 1170 cm^{-1} band) of the 285 cm^{-1} band and the envelope of bands at $310\text{--}350\text{ cm}^{-1}$.