AFOSR - TR - 72 - 0292

AD736882

FINAL REPORT

from

LIQUID CRYSTAL INSTITUTE
KENT STATE UNIVERSITY

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

DDC
RECEIVED
FEB 14 1972
D

ARPA Order Number - 1003

Program Code Number - 7M10

Name of Contractor - Air Force Office of Scientific Research

Date of Contract - June 1, 1967

Amount of Contract - $197,316.00

Approved for public release;
distribution unlimited.

Contract Number - F44620-67-C-0103

Principal Investigator - Glenn H. Brown

Telephone Number of Principal Investigator - (216)-672-2654

Contract Expiration Date - November 30, 1971

Project Scientist - Glenn H. Brown

Short Title of Work - "Basic Studies of Liquid Crystals as Related to Electro-Optical and Other Devices"

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

January 28, 1972
Date

Glenn H. Brown
Glenn H. Brown, Director
Liquid Crystal Institute
Principal Investigator on Project

56

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Liquid Crystal Institute
Kent State University
Kent, Ohio 44240

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

BASIC STUDIES OF LIQUID CRYSTALS AS RELATED TO ELECTRO-OPTICAL AND OTHER DEVICES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Scientific Final

5. AUTHOR(S) (First name, middle initial, last name)

Glenn H. Brown

6. REPORT DATE

January 1972

7a. TOTAL NO. OF PAGES

55

7b. NO. OF REFS

10

8a. CONTRACT OR GRANT NO.

F44620-67-C-0103

b. PROJECT NO.

1003

c. 61102F

d. 681303

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES

TECH, OTHER

12. SPONSORING MILITARY ACTIVITY

AF Office of Scientific Research NC
1400 Wilson Blvd.
Arlington, Va. 22209

13. ABSTRACT

The research performed in the Liquid Crystal Institute was devoted to structure determination, synthesis, and theoretical and fundamental properties of liquid crystals, including such properties as optical and thermal. The structure studies were carried out using x-ray, Mössbauer and nuclear magnetic resonance techniques. The theoretical aspects of the research concerned models of liquid crystalline structures and a better insight into inelastic scattering and deformation of polarized light by liquid crystalline systems. The synthetic work was especially related to the preparation of new compounds which exhibited new phases of liquid crystallinity. In addition to the preparation of new compounds, the synthetic program was used to prepare known compounds for studies relating to structure and other fundamental properties of the liquid crystalline state of matter.

This contract is rather unique in that it presented the "first" in a variety of research activities on the liquid crystalline state of matter. The first nmr studies on molecular configuration in liquid crystalline systems was reported. The first Mössbauer studies on liquid crystals were performed and the result published. Also in this laboratory new liquid crystalline phases were first observed. These included a new nematic phase and new smectic phases different from those which had been reported by others working in liquid crystals.

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

TABLE OF CONTENTS

		Page
SECTION I	Personnel	1
SECTION II	Introduction	2
SECTION III	Theoretical Studies	4
SECTION IV	Molecular Structure and Physical Properties of Thermotropic Liquid Crystals	21
SECTION V	Nuclear Magnetic Resonance Studies	22
SECTION VI	Synthetic Studies	24
SECTION VII	Optical and Thermal Properties of New Liquid Crystalline Compounds	31
SECTION VIII	Use of Liquid Crystals As Reaction Media	35
SECTION IX	Mössbauer Studies	48
SECTION X	Structural Studies by Use of X-ray Methods	50
SECTION XI	Conclusions	52
SECTION XII	Journal Publications Under This Contract	53

Personnel

A number of persons worked on the project. They are identified as follows:

Name	Position	Area of Research
Brown, Glenn H.	Project Director Regents Professor Director, Liquid Crystal Institute	X-ray and Solvent Media
Wu, Sheila	Research Assistant	Optical and Thermal Properties, Synthesis
Uhrich, D.L.	Associate Professor of Physics	Mössbauer Laboratory
Taylor, T.R.	Postdoctoral Fellow	Optical and Thermal Properties
Saupe, Alfred	Professor of Physics, Research Associate	Theory and Optical Properties
Neumann, D.L.	Postdoctoral Fellow (8 months)	Liquid Crystals as Solvents
Lesser, David	Research Assistant	X-ray
Lee, Y.S.	Postdoctoral Fellow (2 months)	Liquid Crystals as Solvents
Fergason, J.L.	Research Associate, Associate Director of Liquid Crystal Institute	Optical and Thermal Properties
Doane, J.W.	Associate Professor of Physics	NMR
Bravo, N.	Research Assistant	NMR
Bacon, W.E.	Research Associate	Liquid Crystals as Solvents
Arora, S.L.	Research Associate	Optical and Thermal Properties, Synthesis

Introduction

This contract was carried out in conjunction with the Westinghouse Corporation. It was the responsibility of the Liquid Crystal Institute of Kent State University to focus on fundamental research while the Westinghouse Corporation was to carry out fundamental research as well as some applied research in an attempt to discover applications of the liquid crystalline state of matter.

The research performed in the Liquid Crystal Institute was devoted to structure determination, synthesis, and theoretical and fundamental properties of liquid crystals, including such properties as optical and thermal. The structure studies were carried out using x-ray, Mössbauer and nuclear magnetic resonance techniques. The theoretical aspects of our research concerned models of liquid crystalline structures and a better insight into inelastic scattering and deformation of polarized light by liquid crystalline systems. The synthetic work was especially related to the preparation of new compounds which exhibited new phases of liquid crystallinity. In addition to the preparation of new compounds, the synthetic program was used to prepare known compounds for studies relating to structure and other fundamental properties of the liquid crystalline state of matter.

This contract is rather unique in that it presented the "first" in a variety of research activities on the liquid crystalline state of matter. The first nmr studies on molecular configuration in liquid crystalline systems was reported. The first Mössbauer studies on record were initiated with this contract and have since been carried on under Contract #44620-69-C-0021 with some very interesting results having been recorded in the scientific literature. This contract saw an advancement in our understanding of

inelastic scattering properties of liquid crystals and also enhanced our knowledge of the deformation of polarized light by liquid crystalline systems. Under this contract, new liquid crystalline phases were first observed. These included a new nematic phase and new smectic phases different from those which had been reported by others working in liquid crystals.

In addition to the scientific reports written under this contract, 10 papers were published in the scientific literature. These papers are listed in Section XII.

Theoretical Studies

The theoretical studies were done by Dr. Alfred Saupe with help from his colleague Dr. Jurgen Nehring. These studies were addressed to the subjects of the deformation of nematic liquid crystals by polarized light and the alignment singularities in nematic liquid crystals.

I. Deformation of Nematic Liquid Crystals by Polarized Light.

Experimental studies show the existence of a torque density in linearly polarized light waves that propagate in anisotropic matter (nematic liquid crystals). The following pages written by Dr. Saupe on the deformation of nematic liquid crystals by polarized light states the subject clearly. Some consequences of the energy-stress tensor of the electromagnetic field are also presented. It seems within reason that the experiments explained in this description by Dr. Saupe can be improved to obtain quantitative measurements of the torque density.

The description by Dr. Saupe of the deformation of a nematic liquid crystal by polarized light follows:

Nematic liquid crystals formed by organic substances show a strong optical anisotropy. The anisotropy is due to a partial parallel orientation of the elongated molecules. Optically the liquids behave like uniaxial crystals with the axis parallel to the preferred orientation.

Connected with the parallel orientation are elastical properties[1]. The state of lowest energy corresponds to a uniform parallel orientation. In a deformed nematic liquid the preferred orientation changes continuously in space. The deformations have strong optical effects which can be used to observe torque densities in electromagnetic waves. No direct observation

of such a torque density has so far been reported to our knowledge†. The existence of a torque density implies that energy and momentum flow have different directions and the subject touches questions connected with the old Abraham-Minkowski controversy. (See for instance M. V. Laue[2])

For an estimation of the light intensity that is necessary to cause an observable deformation, we regard a plane nematic layer of thickness z_o, in the x,y-plane of a cartesian coordinate system. Without outside interaction the molecules shall align parallel to the z-axis because of a surface action that enforces a normal orientation of the surface layer. The torque density due to the presence of an electromagnetic field is given by:

$$(1) \qquad t_{em} = -\frac{1}{4\pi}(\mathbf{E} \times \mathbf{D}) - \frac{1}{4\pi}(\mathbf{H} \times \mathbf{B}) = -(\mathbf{E} \times \mathbf{P}) - (\mathbf{H} \times \mathbf{M})$$

if we assume that Maxwell's stress tensor is valid. With a homogeneous magnetic field parallel to x the layer remains undeformed until H reaches a critical value $H_o = \sqrt{\frac{K_3}{\Delta\chi}}\,\frac{\pi}{z_o}$. K_3 is the elastic constant for bent deformations in the liquid crystal. The difference in diamagnetic susceptibility parallel and perpendicular to the optical axis $\Delta\chi = \chi_1 - \chi_2$ is assumed to be positive. For H slightly larger than H_o the layer is deformed and the difference in path length between ordinary and extraordinary ray for normal incidence becomes:[3]

$$(2) \qquad \delta = z_o n_o \frac{n_e^2 - n_o^2}{n_e^2}\,\frac{K_3}{K_1}\,\frac{H-H_o}{H_o}$$

K_1 is the elastic constant for splay, n_e and n_o are the principle refractive indices for the light with which the layer is observed. When in addition

---

†Measurements of the resulting total torque as a double refracting plate transmitted by polarized light have been made earlier. (R.A. Beth, Phys. Rev. 50, 115 (1960))

to the static magnetic field a weak alternating electric field in x direction of a sufficiently high frequency is present, we have to replace H by $H + \Delta\varepsilon\langle E^2\rangle/8\pi\Delta\chi H$. Especially for $H = H_o$ we obtain:

$$\delta = z_o^3 n_o \frac{n_e^2 - n_o^2}{n_e^2} \frac{\Delta\varepsilon\langle E^2\rangle}{8\pi^3 K_1} \quad . \tag{3}$$

With the known elastic constants and refractive indices for nematic liquid p-azoxyanisole[3,4], we obtain the following result: When a layer of 1.5×10^{-2} cm thickness of p-azoxyanisole at 120°C is observed with green mercury light and a normally incident linear polarized plane wave with $\lambda = 633$ mμ is used to induce deformations, an intensity of 1 watt/cm^2 is needed for a deformation that causes the phase shift $\delta = \lambda$.

The magnetic field of the wave can be neglected since $\Delta\chi$ is many orders of magnitude smaller than $\Delta\varepsilon$. Also deformation effects caused by the mercury light can be neglected because its intensity can be kept very much smaller than 1 watt/cm^2. Our estimation shows that light of a moderately high intensity will cause observable deformations. Qualitative observations of the effect can easily be made with a focused laser beam.

For the actual observations (Fig. 2-3) a mixture of 98% p-azoxyanisole and a 2% α-methoxycinnamic acid (by weight) was used. This mixture gives easily a normal orientation between glass plates and the physical properties of its nematic phase are still similar to pure p-azoxyanisole. The thickness of the layer was near 1.7×10^{-2} cm and the temperatures were between 120-130°C. The experimental setup used for Fig. 2 is shown in Fig. 1. A He-Ne laser with an output of about 15mW at 636 mμ was focused on the layer. The focus spot had a mean width of about 0.5×10^{-2} cm. The layer was observed between crossed polarizers using the green mercury line. Some of the scattered laser light penetrated the interference filter and caused the chain of bright spots on Fig. 3.

Fig. 2a and 2b were obtained with the same magnetic field (~500 Gauss) and with the laser beam focused to the same spot. The polarization is in 2b nearly parallel to the magnetic field and six nearly circular fringes appear that indicate the deformation of the liquid crystal. The effect is evidently not caused by an increase in temperature due to light absorption since it disappears when the polarization is normal to the magnetic field (Fig. 2a).

Fig. 3 was obtained with an arrangement like that shown in Fig. 1 but the layer has been turned by 30° so that the angle between the normal of the layer and the laser beam axis increased to around 40°. The deformations are here induced by light alone. With the polarization parallel to the plane of incidence an increase of the birefringence is observed which indicates that the molecules are again somewhat turned towards the electric field. It can easily be demonstrated that the birefringence is actually increased; applying a magnetic field in the plane of incidence and normal to the axis of observation causes the fringes to move outward. A local temperature increase could lead to a similar picture but due to a decrease in birefringence. Also, no effect can be observed with the electric field normal to the plane of incidence. With more elaborate experiments it should be possible to obtain quantitative values for the torque density in propagating electromagnetic waves.

The existence of a torque density requires, for the conservation of the angular momentum, that a wave packet carries a linear momentum that has not the direction of its propagation, that is, the direction of the energy flow. Our results are qualitatively in agreement with Minkowski's energy-momentum tensor for the electromagnetic field. Minkowski's tensor is defined by:

(4) $$T_{\alpha\beta} = -\frac{1}{4\pi}(E_\alpha D_\beta + H_\alpha B_\beta) + \delta_{\alpha\beta} W$$

$$T_{4\alpha} = \frac{i}{c} S_\alpha \quad , \quad T_{\alpha 4} = icg_\alpha \quad , \quad T_{44} = -W$$

We follow the convention that Greek subscripts run over the space coordinate (1,2,3), while Latin subscripts run over all 4-coordinates (x_4 = ict) and use in eq. (4) the abbreviations $W = \frac{1}{8\pi}(\underset{\sim}{E}\underset{\sim}{D} + \underset{\sim}{H}\underset{\sim}{B})$, $S = \frac{c}{4\pi}(\underset{\sim}{E} \times \underset{\sim}{H})$, and $g = \frac{1}{4\pi c}(\underset{\sim}{D} \times \underset{\sim}{B})$ stands for Minkowski's momentum density. We assume a real and linear relation between $\underset{\sim}{E}$ and $\underset{\sim}{D}$ and $\underset{\sim}{H}$ and $\underset{\sim}{B}$.

Minkowski's momentum density includes a mechanical contribution. The proper momentum density of the field is given by Abraham's expression $g = S/c^2$. This has been demonstrated explicitly for a number of examples[5,6] and was also experimentally confirmed[7]. The inclusion of a mechanical momentum can, however, not be avoided if the tensor is to account for a torque density in a uniform continuum.

Although Minkowski's tensor includes mechanical quantities and is not the proper tensor of the electromagnetic field, it seems to be appropriate for waves propagating in a continuum. In fact important arguments supporting it have been obtained by regarding such waves and we can add additional support by the following considerations.

Minkowski's momentum density is carried by a propagating wave in the sense that momentum flow and momentum density are related in the same wave as energy flow and energy density (eg. (5) and (5a)). V is here the ray velocity.

(5) $$T_{\alpha\beta} = g_\alpha V_\beta$$

(5a) $$S_\beta = W V_\beta$$

The forces that transport the mechanical momentum are the Lorentz forces

due to the polarization currents[8]. Their force density is given by $\dot{\mathfrak{g}} - \dot{\mathfrak{S}}/c^2 = (\dot{\mathfrak{P}} \times \mathfrak{B} + \mathfrak{D} \times \dot{\mathfrak{M}})/c$.

Equation (5a) provides a strong argument in favor of Minkowski's tensor. It can be shown that the ray velocity defined by this equation follows the addition theorem for velocities of particles[2,10]. Therefore, the row vector T_{4i} is always proportional to the ray vector $A^* = (\mathfrak{V}, ic)/\sqrt{c^2-V^2}$. Eq. (5) is a consequence of this statement since under the transformations $T_{ik} = \alpha_{im}\alpha_{kn}T_{mn}$ each row vector can be transformed in a first step like a normal vector and then linear combinations of these vectors have to be formed that replace the original row vectors. All row vectors are, therefore, parallel to A^*, if one of them remains always parallel to it. It follows further that the column vectors are also parallel to each other, and, as is mentioned by Shockley[6], that we can write $T_{ik} = a_i b_k$.

In Minkowski's tensor for a propagating wave (a_i) is proportional to the wave number vector $A = (\frac{\mathfrak{n}}{\lambda}, i\frac{\nu}{c})$ and b_i proportional to the ray vector. We obtain his tensor with $a_i = WA_i/\nu = (\mathfrak{g}, i\frac{W}{c})$ and $b_i = \sqrt{c^2-V^2}\, A^* = (\mathfrak{V}, ic)$. It leads to

$$T_{ik} = \sqrt{c^2-V^2}\,\frac{W}{\nu}\,A_i A_k^* \quad . \tag{6}$$

The factor $\sqrt{c^2-V^2}\,(W/\nu)$ is invariant since T is a tensor. It is possible to give this fact a physical interpretation:

Let us regard a volume element that moves with the ray velocity. Its volume in any inertial system is $\tau = \tau_o\sqrt{1-V^2/c^2}$ when τ_o is the volume in its rest system (V = 0). The energy contained in τ divided by $h\nu$ may be called the number of photons in τ, for it is equal to $(\tau_o/c^2)\sqrt{c^2-V^2}(W/h\nu)$ and remains constant under Lorentz transformations.

Minkowski's tensor for propagating waves has an interesting simple structure and contrary to earlier assumptions[9] it is compatible with the

quantum concept of light. In real matter, however, we cannot expect that eq. (1) which is directly connected with Minkowski's tensor is strictly valid. Real matter cannot be treated like a uniform continuum when forces and torque densities are regarded. In the case of liquid crystals where we can neglect an electronic band structure, it seems more appropriate to regard individual molecules and avoid the continuum approach. The torque on a molecule, that has an (induced) dipole moment $\mathfrak{P}_i$ and that is subjected to a homogeneous field $\mathfrak{E}_i$, is given by $-(\mathfrak{E}_i \times \mathfrak{P}_i)$. This leads to the torque density $-(\mathfrak{E}_{loc} \times \mathfrak{P})$, where $\mathfrak{E}_{loc} = \mathfrak{E} + \Delta\mathfrak{E}$ is an average local field. Eq. (1) remains valid when ΔE is parallel to P but because of the anisotropy of the crystal this is not generally the case. The Lorentz forces, which, as we have seen, are of importance for the momentum transport, have no influence on the torque density when the wavelength is large against molecular dimensions. Their value also may change due to local field corrections and, therefore, the momentum flow density. Contrary to energy density and energy flow, the momentum density and the momentum flow, including the mechanical momentum transported with the wave is, therefore, not completely determined by macroscopic properties (see also ref. 6) and the molecular structure of the material has to be taken into account.

REFERENCES

1. See for instance: F.C. Frank, Disc. Farad. Soc. **25**, 19 (1958).
2. M.V. Laue, Z. Physik **128**, 387 (1950); "Die Relativitätstheorie" 1. Band, Friedr. Vieweg & Sohn Braunschweig 1955.
3. A. Saupe, Z. Naturforschg. **15a**, 815 (1960).
4. P. Chatelain, Dissertation, Paris 1937; Bull. Soc. Minéralog. franc. **50**, 280 (1937).
5. N.L. Balazs, Phys. Rev. **91**, 408 (1953).

6. W. Shockley, Proc. Nat. Ac. Sc. 60, 807 (1968).

7. R.P. James, N.A.S. Proceedings 61, 1149 (1968).

8. G. Gyorgyi, Amer. J. Phys. 28, 85 (1960).

9. W. Shockley and R.P. James, Phys. Rev. Letters 18, 876 (1967); Science 156 (3747), 542 (1967).

10. C. Miller, "The Theory of Relativity", Oxford University Press, 1966.

FIGURE 1

Experimental setup for the observation of deformation effects. Laser light with $\lambda = 633$ mμ is focused on the liquid crystal layer. The interference filter is selective for $\lambda = 546$ mμ.

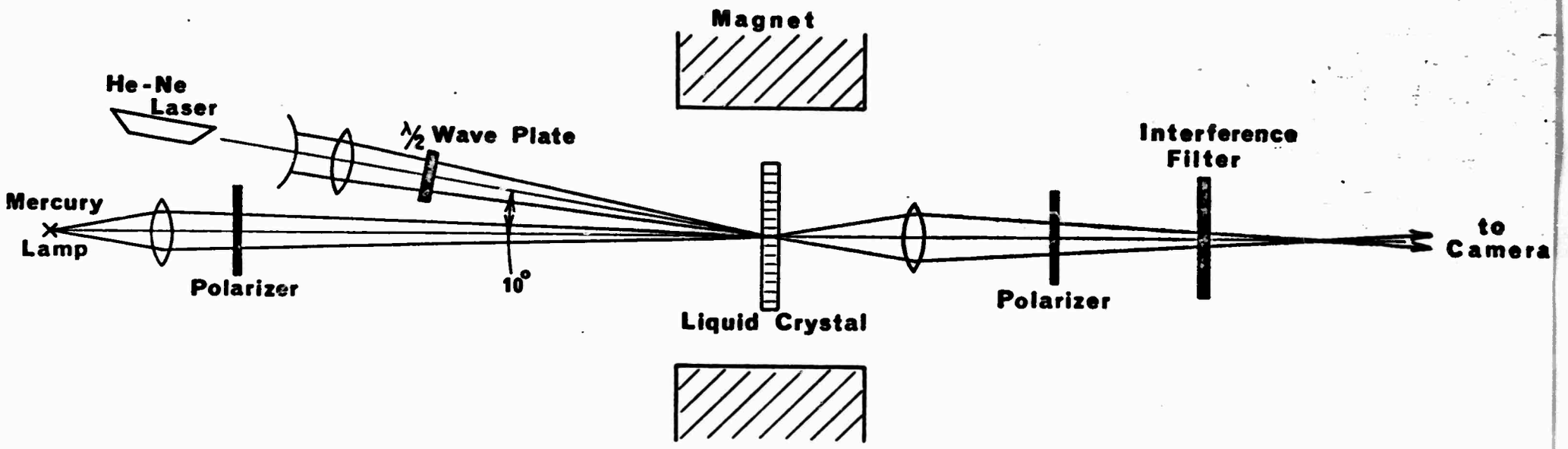

Magnet
He-Ne
Laser
λ/2 Wave Plate
Interference
Filter
Mercury
Lamp
Polarizer
10°
Liquid Crystal
Polarizer
to
Camera

FIGURE 2

Nematic layer between crossed polarizers, approximately normal incidence, x 90. The white line in the upper part is the border against air; it is parallel to the magnetic field.

(a) $E_{laser} \perp H_{magnet}$

(b) $E_{laser} \parallel H_{magnet}$

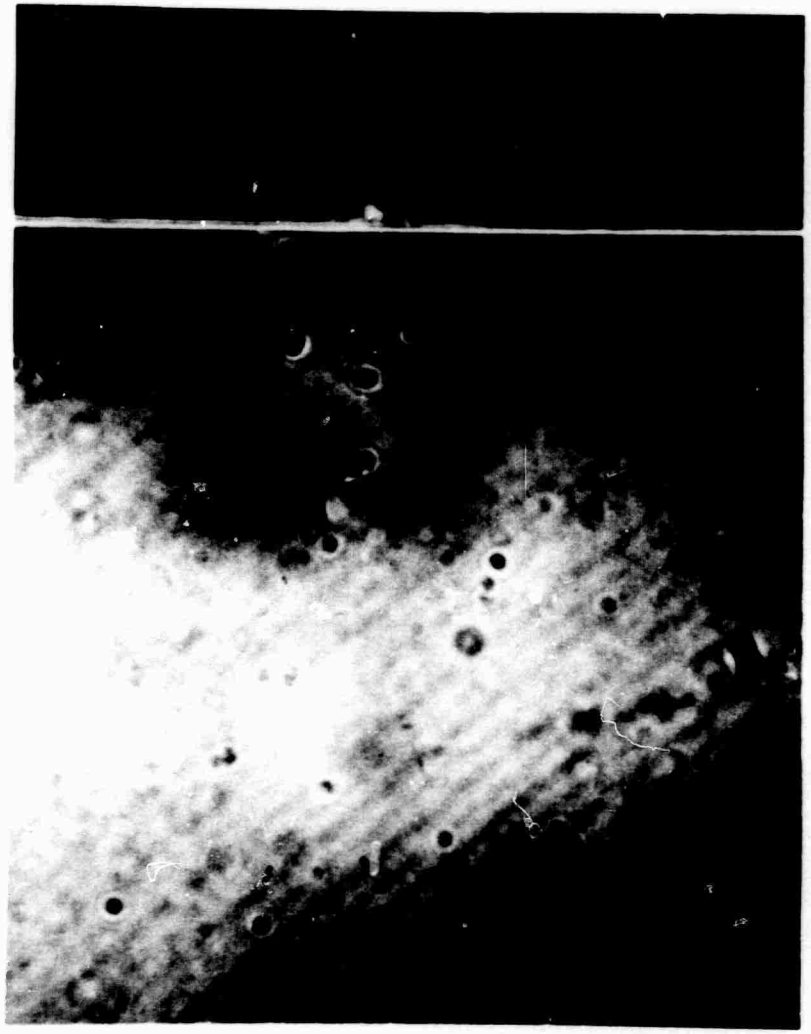
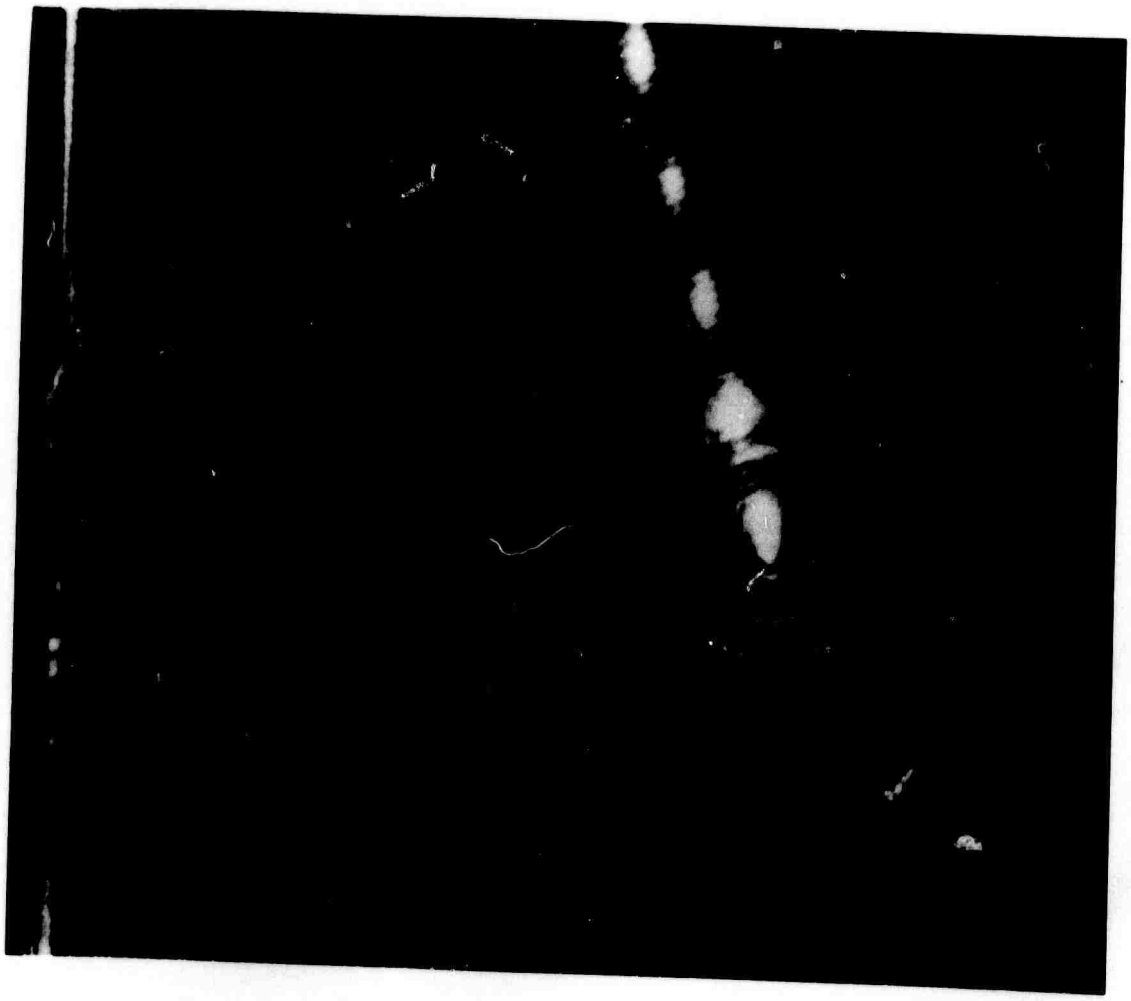


Fig. 2a

Fig. 2b

FIGURE 3

Nematic layer between crossed polarizers, oblique incidence, x 90; E_{laser} parallel to plane of incidence (no magnetic field).



II. Alignment Singularities in Nematic Liquid Crystals.

The theoretical and experimental studies on alignment singularities in nematic liquid crystals were considered under this contract. The basis for the theoretical treatment is the hydrostatic theory of liquid crystals. The usually accepted formulation of this theory was developed by Frank. In this formulation there are, however, some terms neglected without justification. We renewed, therefore, the derivation and comprised Oseen's molecular approach with a formalized phenomenalogical approach. The derivation and the results were published in The Journal of Chemical Physics 54, 337 (1971).

An abstract of the paper on alignment singularities in nematic liquid crystals can be summarized as follows:

Simple derivations of the elastic theory of liquid crystals with uniaxial molecular order are given using a molecular Cauchy-like approach and a more general phenomenological approach. In a second-order approximation, both methods lead to the same expression for the electric energy density, except for the existence of one "Cauchy-relation" between the elastic constants in the molecular case. The phenomenological equation contains nine elastic constants which is two more than in Frank's earlier derivation. The molecular equation is in agreement with Oseen's original expression. Differences between the molecular and the phenomenological approach and the justification of neglecting terms which do not contribute to the Euler-Lagrange differential equation are considered in the journal article.

Higher than second order terms are given for cholesteric liquids. In addition, the consequence of curvature-induced electric polarization for the equilibrium structure of liquid crystals is explained in the article in The Journal of Chemical Physics entitled "On the Elastic Theory of Uniaxial Liquid Crystals".

III. Reflection Bands in a Cholesteric Liquid Crystal as a Function of the Angle of Incidence.

Dr. A. Saupe also did some studies of optical properties of planar cholesteric structures. This work was not completed during the life-time of the contract but a few developments did take place which may be of practical interest.

When light propagates from an optically dense medium into the liquid crystal a normal total reflection takes place for angles of incidence larger than a critical angle. For planar cholesteric structures with the interface normal to the twist axis, two critical angles occur. We denote the refractive index of the outside medium by n_a and we assume that the untwisted cholesteric liquid crystal is optically uniaxial with the principle dielectric constants ε, ε_2, $\varepsilon_3 = \varepsilon_2$. We assume further that $\varepsilon_1 > \varepsilon_2$. For the smaller critical angle we have

$$\sin \gamma' = \sqrt{\varepsilon_2}/u_a$$

The observation of this angle allows the determination of ε_2. The information contained in the second critical angle is more complicated.

It was assumed by earlier workers that instead of the above equation one should use $\sin \gamma' = \sqrt{\varepsilon_1}/u_a$. This is wrong and some of the refractive indices of cholesterics available in the literature should be corrected. The correction is easy for measurements at wavelengths equal to or larger than the pitch p of the cholesteric structure. In this case the relation between the second critical angle and the dielectric constants is

$$\sin^2\gamma'' = \frac{\varepsilon_2}{u_a}\left(1 + \frac{\beta^2}{\delta(\lambda/\sqrt{\varepsilon}p)^2} + \ldots\right) .$$

The following approximations have been used here $\varepsilon = (\varepsilon_1 + \varepsilon_2)/2$ and $\beta = (\varepsilon_1 - \varepsilon_2)/2\varepsilon$. It is assumed that $\lambda > \sqrt{\varepsilon}p/3$ and that terms proportional to β^4 can be reflected.

SECTION IV

Molecular Structure and Physical Properties of Thermotropic Liquid Crystals

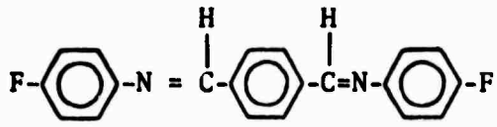
One of the interesting papers originating from this contract was written by Dr. A. Saupe and published as part of the proceedings of the Second International Liquid Crystal Conference. The paper was published in Molecular Crystals and Liquid Crystals 7, 59 (1969) and is entitled "On Molecular Structure and Physical Properties of Thermotropic Liquid Crystals".

A synopsis of that paper may be summarized briefly as follows:

Some models for the molecular structures of liquid crystals including a ferroelectric liquid are discussed in some detail. It is shown that a smectic liquid with a layered structure, in which the preferred orientation of the molecular axis is inclined against the layers, has some similarities with a nematic liquid. Such a tilted smectic liquid may also have a twisted modification corresponding to a twisted nematic or cholesteric liquid crystal. A proposal is made for its molecular structure in which a fairly regular, lattice-like arrangement of alignment singularities is assumed. Twist waves in nematic liquids are regarded and numerical estimations are made for their wave velocity and damping in the nematic liquid, p-azoxyanisole. It is concluded that the damping is too strong for an observation of such waves.

Nuclear Magnetic Resonance Studies

Some work on the structure of liquid crystals was done under this contract using broadline nuclear magnetic resonance procedures. The compound studied was terephthal bis(p-aminofluorobenzene),



in the nematic liquid crystalline state. From line-shape studies of the proton and fluorine nuclear magnetic resonances, we have found that, even through the molecule undergoes thermal oscillations and diffusion, it has a ridged structure indicating that it can pack with other molecules into groups exhibiting the short-range order suggested by current theories. More specifically, we have found that the double-bond linkages on the molecular axis prevent free rotation of the benzene rings with respect to one another, forming a molecule with somewhat of a "spiral" appearance.

We have also found remarkable agreement in the degree of order in this nematic system when measured from the second moment of the fluorine spins and from a characteristic splitting in the proton resonance lines. This is quite significant because it enables us to study the order in other nematic systems where the fluorine has been replaced by other halogens.

The fluorine and proton spin resonances in the nematic liquid crystal state of terephthal-bis-(aminofluorobenzene) were studied using the method of moments. The second moment of the proton line has a large dependence on the molecular configuration as well as on the degree of molecular order. The fluorine second moment, on the other hand, has a negligible dependence on the configuration and is used to obtain a measure of the order. With the degree of order known, the second moment of the proton resonance is used to

examine the possible configurations the molecule may follow. The results rule out the possibility of a planar molecule as well as a molecule in which the aromatic rings and the -N=CH- linkage groups are allowed to rotate around their bonds in an unhindered fashion. Best agreement with the data is found for the case where the plane containing the linkage group makes a preferred angle near 20° relative to the plane of the terminal aromatic rings. The temperature dependence of the proton spectrum is also interpreted in terms of the molecular order.

The details of this study were published in J. Chem. Phys. 50, 1398 (1969) in a paper entitled "NMR Study of Molecular Configuration and Order in a Fluorinated-Liquid Crystalline Schiff Base" by N. Bravo, J.W. Doane, S.L. Arora and J.L. Fergason. This research was continued under Contract No. F44620-69-C-0021.

Synthetic Studies

Two kinds of synthetic work were performed. The first kind was the preparation of known compounds which were used for studying the structural and physical properties of liquid crystals (e.g., nmr studies and x-ray). The second kind of synthesis was the preparation of compounds which had special uses such as solvents for the study of selected chemical reactions. The common compounds which were prepared are cholesteryl nonanoate, p-azoxyanisole and terephthal bis(p-fluoroaniline). These compounds were used in such observations as optical and thermal effects and nuclear magnetic resonance.

A collection of ester derivatives of terephthalic acid and c-hexanedicarboxylic acids were prepared. Some of these new compounds were used for nuclear magnetic resonance measurements and as solvents for studying chemical reactions. These compounds are listed in Tables 1 and 2, along with their transition temperatures. These compounds are relatively simple, have large temperature ranges in the liquid crystalline structure and allow for both proton and halogen resonance studies. Some of them are ideal as solvents for kinetic and mechanism studies, especially di(p-methoxyphenyl)trans-cyclohexane-1,4-dicarboxylate. We also prepared some sulfur containing liquid crystalline compounds. Data on these compounds are given in Table 3. We did not use the compounds for further studies.

The synthesis of the terephthalates and c-hexanedicarboxylic acids were undertaken with a three-fold purpose in mind:

(a) to investigate these two series as basic structures for liquid crystalline formation and to extend their useful range by introducing various groups in the para position in the benzene ring.

(b) to prepare a mesomorphic compound having a mesophase between 140-250°C for evaluation as a substrate to measure the influence of the nematic mesophase on chemical reactions.

(c) to evaluate the mesophase formed by this type of compound as a substrate in chromatographic columns.

In reference to (a) we completed the synthesis of two groups of esters and evaluated them as liquid crystalline compounds (see Tables 1 and 2). It is apparent from the tables that the terephthalate esters show mesophases at a higher temperature than the c-hexanedicarboxylates.

The selection di(p-methoxyphenyl)trans-cyclohexane-1,4-dicarboxylate and the dichloro derivative as nematic solvents for evaluation under (b) has been made. This work is discussed in Section VIII.

These compounds were not tested as stationary phases in chromatography.

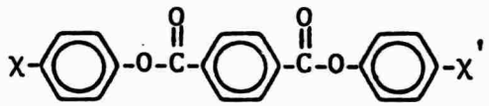
Several liquid crystalline compounds containing mercury (II) were synthesized. These compounds are among the first organo-metallic compounds showing liquid crystallinity to be synthesized. The drawback for these compounds is their lack of thermal stability.

Five bis(p-n-alkoxybenzylidene-4-aminophenyl)mercury(II) compounds were prepared; these compounds were the methoxy, n-propoxy, n-butyloxy, n-hexyloxy, and n-octyloxy members of the homologous series. All five homologs possess a nematic mesophase but the n-butoxy, n-hexyloxy and n-octyloxy homologs possess smectic mesophases as well. Solid-solid transitions were also observed for the three highest molecular weight homologs. The different phases were identified under a polarizing microscope. Thermodynamic data such as temperatures and changes in enthalpy and entropy values at phase transitions were determined by differential thermal analysis. The enthalpy

of transition and change in entropy values were found to be the largest at the solid-nematic or solid-smectic transition. This corresponds to the large energy required to weaken the major intermolecular attractive forces. Thermodynamic data at the nematic-isotropic liquid transition could not be determined quantitatively because all five compounds "melted" with decomposition. A correlation of transition temperatures of the mercury series synthesized with that of the 4,4'-di(p-n-alkoxybenzylideneamino)biphenyl series reported by Gray was made. The thermal stability is lowered by the presence of a mercury atom in the center of the molecule, but the appearance of mesophases and the changing trend while ascending the homologous series remained.

TABLE 1

Disubstituted Diphenyl Terephthalates



X	X'	C-I* Point	C-S** Point	C-N*** Point	N-I**** Point	Comment
H	H	197				Not liquid crystalline
CH_3	CH_3			194	209	
CH_3O-	CH_3O-			207	279	
C_2H_5O-	C_2H_5O-			216	269	
n-C_4H_9O	n-C_4H_9O			185	235	
CH_3O-C(=O)-	CH_3O-C(=O)-	165				Not liquid crystalline
C_2H_5O-C(=O)-	C_2H_5O-C(=O)-			187	235	
n-C_3H_7O-C(=O)-	n-C_3H_7O-C(=O)-		130	205	218	
n-C_4H_9O-C(=O)-	n-C_4H_9O-C(=O)-		138		188	Smectic phase 188° is transition of smectic to isotropic
F	F	225				Not liquid crystalline
Cl	Cl			195	226	
Br	Br			228	230	

Table 1 (continued)
Disubstituted Diphenyl Terephthalates

X	X'	C-I* Point	C-S** Point	C-N*** Point	N-I**** Point	Comment
I	I	284				Not liquid crystalline
Cl	F			182.5	172	Monotropic
NO_2	NO_2			246	235	Monotropic
CH_3O	C_6H_5			165	175.5	
C_2H_5	n-C_8H_{17}			178	184	

* C-I is the crystal-isotropic point

** C-S is the crystal-smectic point

*** C-N is the crystal-nematic point

**** N-I is the nematic-isotropic point

TABLE 2

Disubstituted Diphenyl Cyclohexanedicarboxylates

X	X'	C-I* Point	C-S** Point	C-N*** Point	N-I**** Point	Comment
H	H	154				Not liquid crystalline
F	F			149	119	Monotropic
Cl	Cl			150	186	
Br	Br			163	193	
I	I					Not liquid crystalline
CH_3	CH_3			172	186	
C_2H_5	C_2H_5			107	153	
n-C_3H_7	n-C_3H_7			112	159	
CH_3O	CH_3O			142	236	
CH_3O	C_2H_5			135	230	
$C_2H_5O-C(=O)-$	$C_2H_5O-C(=O)-$			155	196	
NO_2	NO_2	216-219				Not liquid crystalline

* C-I is the crystal-isotropic point

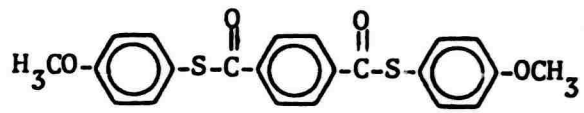
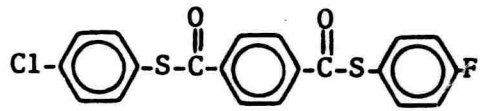
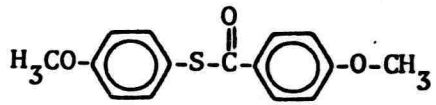
** C-S is the crystal-smectic point

*** C-N is the crystal-nematic point

**** N-I is the nematic-isotropic point

TABLE 3

Sulfur Containing Liquid Crystalline Compounds

Compound	Formula	C-I* Point	C-N** Point	N-I*** Point
bis(4-Methoxyphenyl)thioterephthalate			199	283
4-Chlorophenyl-4'-fluorophenyl thioterephthalate		182.5°		
S-4-Methoxyphenyl-4-methoxythiobenzoate			115	130

* C-I is crystal-isotropic point

** C-N is crystal-nematic point

*** N-I is nematic-isotropic point

SECTION VII

Optical and Thermal Properties of New Liquid Crystalline Compounds

The primary purpose of the studies on the optical and thermal properties of liquid crystals was to better understand these properties in smectic phases and the polymorphism of smectic morphology. These studies may be categorized into three groups.

1. Biaxial Liquid Crystals.

A number of compounds exhibiting nematic and smectic C phases were studied optically using convergent light. The nematic phases were uniaxial but it was shown that the smectic C phases were biaxial with an optic axial angle on the order of 20°. The tilt angles of all smectic C phases observed were 45° within experimental error. A preferential alignment of the molecular axes non-parallel to the containing surfaces was found for the nematic phase. The results of the study are given in detail in the paper entitled "Biaxial Liquid Crystals" which was published in Physical Review Letters **24**, 359 (1970).

2. 4-n-Alkoxybenzylidene-4'-aminopropiophenones.

A homologous series, of the above compounds, was synthesized and their optical and thermal properties studied. The homologues with alkoxy chain C_4 through C_{14} show two smectic phases using thermal methods but optically appear to have only one smectic A phase. We have given an explanation for this unusual behavior in terms of a possible change in "polar" ordering of the smectic A phase.

The complete results of the study are given in the paper entitled "Polymorphism of Smectic Phases with Smectic A Morphology" published in "Liquid Crystals and Ordered Fluids", editors, J.F. Johnson and R.S. Porter, Plenum Press, New York, 1970, p. 321.

3. Alkoxybenzylidene-aminoacetophenones.

A homologous series, of the above compounds, was synthesized and their optical and thermal properties studied. These compounds are of special interest because they show a wide temperature range of smectic A below 130°C and are of interest for study by other techniques such as nuclear magnetic resonance. Many of these compounds show two smectic phases; one being monotropic. The two smectic phases are of type A and optically indistinguishable. Their behavior is similar to that of the compounds in group 2 presented above and hence the polymorphism of smectic A phases is not just peculiar to the compounds of group 2. The hypothesis of "polar" ordering is advanced as an explanation for the two smectic A phases.

The paper entitled "Mesomorphic Properties of Alkoxybenzylidene-aminoacetophenones" presents the results of this study and were published in the Journal of Organic Chemistry 35, 1705 (1970).

4. Phenylenediamine Derivatives.

In another series of optical studies on phenylenediamine derivatives, two liquid crystalline phases with nematic morphology were prepared and studied for optical and thermal properties. A brief synopsis of these studies is as follows:

Bis-(4'-n-alkoxybenzal)-2-chloro-1,4-phenylenediamines and bis-(4'n-alkoxybenzal)-2-methyl-1',4-phenylenediamines with different alkoxy groups have been synthesized. Similar compounds with fluoro, bromo and chloro groups replacing the alkoxy groups have also been prepared. All the compounds show a nematic liquid phase.

An additional lower temperature liquid crystalline phase is observed with chloro-substituted compounds for n-alkoxy chain lengths of C_8 and longer

and with the methyl substituted compounds for chain lengths of C_{10} and longer. This lower temperature phase can show a threaded texture very similar to the nematic phase. Furthermore, both phases can be uniformly oriented by surface action and can assume a twisted structure. We suppose that the lower temperature phase has a layered structure in which the molecules are inclined to the layers, and that it corresponds to a smectic liquid crystal classified by Sackmann and Demus as smectic C.

A paper on this study was published in Molecular Crystals and Liquid Crystals 10, 243 (1970).

5. Optical and Thermal Properties of Phenylene bis-Alkoxybenzoates.

A study of the optical and thermal properties of phenylene bis-alkoxybenzoates was carried out in order to study the effects of the central carboxyl group on the formation of smectic phases and on the thermal stability of liquid crystalline phases. A parallel series with a methyl substituent at the 2-position on the 1,4-phenylene ring were also prepared to investigate the effect of a lateral substituent on the mesomorphic properties. These compounds have a nematic phase and in many cases a smectic C phase also.

A number of conjectures concerning the effect of molecular geometry on thermal stability of liquid crystalline phases are drawn from the comparison of thermal data and structure for the 1,4-phenylene bis-4'-alkoxybenzoates and the 2-methyl-1,4-phenylene series. A comparison between the phenylene bis-alkoxybenzoate series and the previously reported[1] bis(4'-n-alkoxybenzal)-1,4,-phenylenediamines was also made.

The 2-methyl-1,4-phenylene bis-4'-n-alkoxybenzoates have lower melting points and higher nematic-isotropic transition temperatures than are commonly encountered in liquid crystalline compounds. Since they are also relatively

inert, they should be of interest as liquid crystalline solvents for a number of physical studies.

This work was published in the Journal of Organic Chemistry **35**, 4055 (1970) in a paper entitled "Molecular Structure and Liquid Crystallinity: Phenylene Bis-Alkoxybenzoates".

REFERENCE

1. Arora, S.L., Taylor, T.R., Fergason, J.L. and Saupe, A., J. Amer. Chem. Soc. **91**, 3671 (1969).

SECTION VIII

Use of Liquid Crystals as Reaction Media

The role of liquid crystals as solvents to study selected chemical reactions is intriguing. The work reported in this section represents some of the very first studies of this interesting new area of scientific research. The possibilities of different reactions to be investigated is quite large and the few we have studied are reported herein. Our studies include the Claisen rearrangement, polymerization reactions and the benzidine rearrangement.

The solvent used for most of these studies was the nematic liquid form of the compound di(p-methoxyphenyl)trans-cyclohexane-1,4-dicarboxylate with a nematic range of 143-242°C. We made a careful study of the Claisen rearrangement of allyl phenyl ethers in this solvent. In the pages in this section which follow, we outline our studies of liquid crystals on solvent media.

A. The Claisen Rearrangement.

The use of liquid crystals as reaction media for the Claisen rearrangement was studied in an effort to determine the influence of the ordered nematic solvent upon the reaction. This work has been completed and it was the subject of two papers one of which was presented at the Third International Liquid Crystal Conference, Berlin, Germany, August 1970. We studied a series of para substituted allyl phenyl ethers which undergo thermal rearrangement. Two types of solvents, namely, nematic and isotropic were selected. The rate constants for the reactions were determined at three temperatures and the thermodynamic parameters were calculated from the Arrhenius equation for each of the systems in the two types of solvents. The following conclusions were drawn from this study:

(a) Allyl *para* substituted phenyl ethers (i.e. NO_2, CN, Cℓ, CH_3) form homogeneous solutions with the nematic solvent; di(*p*-methoxyphenyl) *trans*-cyclohexane-1,4-dicarboxylate.

(b) Claisen rearrangement is a first-order reaction in both types of solvents.

(c) The transition state for the rearrangement reaction shows polar character in both types of solvents.

(d) The rearrangement reactions in the liquid crystal solvent demonstrate the same influence with temperature in the nematic and isotropic phase.

(e) The activation energies, E_a, for each reaction are equivalent within experimental error in the nematic solvent, and in the isotropic solvent, diphenyl ether.

(f) The order and molecularity for the reactions are the same in the two types of solvents.

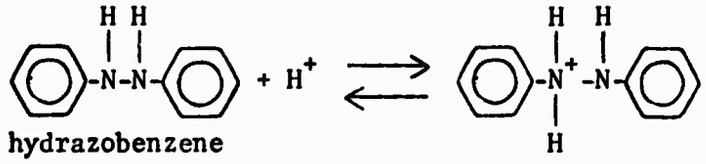
The details of these studies may be found in two papers written by W.E. Bacon and G.H. Brown. They appeared in *Molecular Crystals and Liquid Crystals* **6**, 155 (1969) and **12**, 229 (1971).

B. The Benzidene Rearrangement.

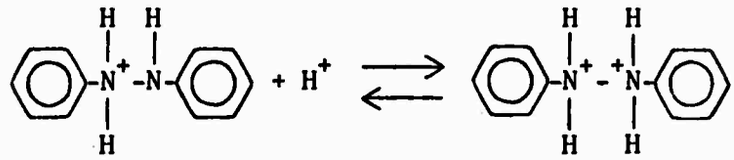
As we approached the end of the contract we attempted to study the benzidene rearrangement in a nematic liquid. No definitive results were obtained, but we feel that the progress made on this project is worth recording as part of the work accomplished under the contract.

The purposes of this investigation are to use liquid crystals as reaction media (1) to identify the chemical reaction mechanism of the benzidine rearrangement of hydrazobenzene, (2) to control the product distribution of this reaction, and (3) to search for some directions of the chemical application of liquid crystals.

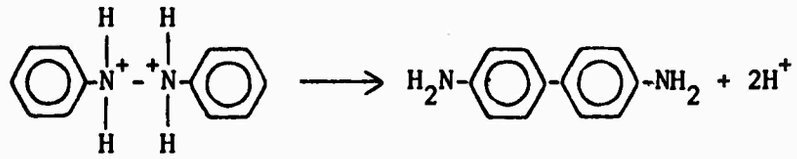
The benzidine rearrangement is acid catalyzed. Three steps had been proposed:



hydrazobenzene (1)

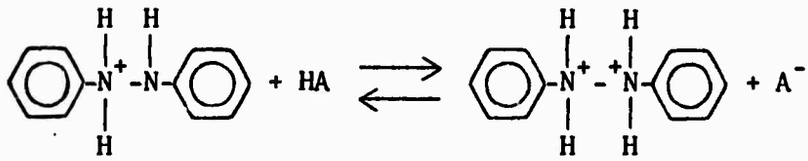


(2)



benzidine (3)

Step (2) is rate determining. This step may also be:



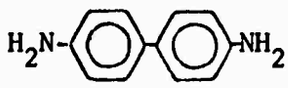
(2')

Because of the existence of the equilibrium of the catalyzing acid:

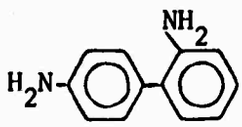
$$HA \rightleftharpoons H^+ + A^- ,$$

one cannot determine whether the mechanism of the rate determining step involves (2) in which a positively charged proton mounts on the second nitrogen, or (2') in which an electrically neutral acid mounts on the second nitrogen and then leaves a proton on this nitrogen.

Concurrent products of the reaction in isotropic media exist in the ratio of 70:30.



70%



30%

Consider that the benzidine rearrangement is carried out in a nematic medium. The dissolved elongated reactant hydrazobenzene molecules should because of the dense molecular packing requirement of the system, lie parallel to the neighboring molecules of the nematic solvent. If the rate determining step of the benzidine rearrangement follows mechanism (2), the variation of the chain length of the catalyzing acid would result in no difference in the reaction rate, since the incoming group that attacks the nitrogen atom is the dissociated proton, H^+. If the mechanism (2') is true, then the reaction rate of the benzidine rearrangement is expected to vary with the chain length of the catalyzing acid. The low reaction rates associated with long chain catalyzing acids are the result of the steric hindrance and mutual position of the reactant and the catalyzing acids in the nematic medium. A successful collision between the nitrogen atom of the undissociated catalyzing acid would require that the environmental structure be distorted to such an extent as to allow the reacting centers to approach each other. A long chain catalyzing acid requires large distortion of the environmental structure and will result in a slow reaction rate and a large activation energy for the reaction.

An intermolecular process is diffusion controlled. The small dynamic anisotropy of the reaction medium will not result in noticeable difference in the kinetics of the process. On the other hand, the diffusion constant of elongated molecules, say, the undissociated catalyzing acid, is a very sensitive function of their length. Thus, an obvious dependence of the reaction rate of the benzidine rearrangement on the chain length of the catalyzing acid will establish the existence of the mechanism (2') in general. Otherwise, the mechanism (2) is true.

It has been reported that the heat of mixing of o-xylene in nematic p,p'-azoxyphenetole is larger than that of the para isomer by about 1000 cal/mol. This might reflect a difference in the isomer distribution in the benzidine rearrangement in the nematic solvent from that in the isotropic solvent. The 70:30 ratio (benzidine:diphenylene) of the concurrent products has been found independent of many properties of isotropic media. This ratio might be thermodynamically distorted by the nematic structure of the reaction medium to favor the high yield of the linear benzidine. If this product distribution will show a ratio considerably different from 70:30, the value in using liquid crystalline media for chemical syntheses is obvious.

2. Results and Discussions

The benzidine rearrangement of hydrazobenzene takes place at a moderate rate ($k \sim 10^{-3}$ mol/liter/min in ethanol at 25°C, $k \sim 10^{-2}$ mol/liter/min in aqueous ethanol at 55°C), depending on the concentration of the catalyzing acid. The same reaction was carried out at 30°C in the nematic medium which is a mixture of 1 mole p-methoxybenzylidene-p-n-butylaniline (MBBA) and 1 mole p-ethoxybenzylidene-p-n-butylaniline (EBBA), nematic range: 0°C to 60°C. The concentration of the hydrazobenzene in the solution was 15% by weight. Acetic acid and benzoic acid were used as catalysts. It was found that the experiment was complicated by the following factors:

(a) The reaction products react rapidly with the nematic solvents which are Schiff's bases.

(b) Similar cases might be expected for EBBA and diphenylene. NMR spectra obtained from a Varian A-60 NMR spectrometer show that the chemical shifts of the protons on the carbon atoms adjacent to the oxygen atoms [i.e., CH_3O-⟨⬡⟩- and CH_3CH_2O-⟨⬡⟩-] in the nematic phase are very

close to those of the amino hydrogens in the reaction products. Their δ-values in chloroform are between 3 and 4 ppm relative to TMS (δ=0).

The complication in (a) could be taken care of by using a nematic solvent which is a non-Schiff's base. The type of room temperature nematic liquid crystals which are stilbene derivatives appear suitable.

The problem in (b) might be solved by the use of a NMR spectrometer of high resolving power. Alternatively, a deuterated alkoxy-group built in the liquid crystal molecule can be considered.

A brief experiment was carried out using a du Pont 900 Differential Thermal Analyzer to follow the kinetics of the benzidine rearrangement of hydrazobenzene in ethanol, with benzoic acid as catalyst. It was observed that a weak exothermic peak starting at about 50°C occurs in the heating thermogram. The peak is weak because the solubility of hydrazobenzene in ethanol is only 4% by weight. However, this signifies that the rearrangement reaction is exothermic. The DTA technique might be a convenient means for kinetic studies of the benzidine rearrangement in a liquid crystal medium, when the solubility of the reactant in the nematic liquid is sufficiently large to give an exothermic peak of analyzable area.

C. Polymerization Reactions in Nematic Liquid Crystalline Solvents.

1. Polymerization of Phenylacetylene.

The polymerization of phenylacetylene in the nematic solvent, di(p-methoxyphenyl)trans-cyclohexane-1,4-dicarboxylate, at 150°, is catalyzed by cumene hydroperoxide. The kinetics of this reaction can be followed by the potentiometric titration of the acidic hydrogen in phenylacetylene with silver nitrate solution as shown in the following equations:

$$HC{\equiv}C\text{-}R + 2AgNO_3 \longrightarrow AgC{\equiv}C\text{-}R \cdot AgNO_3 + HNO_3 \qquad (1)$$

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O \qquad (2)$$

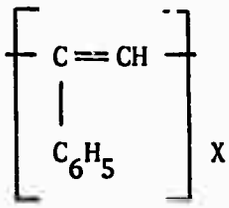
The titration of the nitric acid with standard sodium hydroxide requires a potentiometer equipped with a salt bridge connecting the silver nitrate-phenylacetylene solution with the calomel electrode. This solution is highly colored because of the polyphenylacetylene formed during the polymerization. The change in concentration of phenylacetylene as a function of time follows first-order kinetics provided samples are measured after the induction periods of the reaction. The induction period is typical of a chemical reaction which undergoes a series of consecutive steps. For example, in this polymerization reaction the concentration of the reactive intermediate reaches a maximum during the induction period, and may serve as the rate-determining step. This step corresponds to the formation of the free radical from phenylacetylene. The reaction of the free radical with a molecule of phenylacetylene to yield the polymer is probably a very fast reaction, and therefore, contributes very little to the overall rate determination. Therefore, if the rate of formation of the free radical, that is, the initial step is the rate determining step of the reaction, the influence of the solvent may not be measured. In other words, the rate constant of the initiation step may be independent of the solvent. We determined the rate of decomposition of cumene hydroperoxide in nematic solvents and subsequent comparison with available rate data for this hydroperoxide in isotropic solvents at 150°. The results of this work added information to the role of the nematic solvent, i.e., di(p-methoxyphenyl)trans-cyclohexane-1,4-dicarboxylate, on the rate of decomposition of cumene hydroperoxide.

The completion of a series of polymerization reactions with phenylacetylene catalyzed with cumene hydroperoxide indicated that the rate of

polymerization increases as the concentration of the cumene hydroperoxide increases. These results indicate that polymerization of phenylacetylene with cumene hydroperoxide is a second-order reaction and this reaction might best be studied by following the change in concentration of phenylacetylene and cumene hydroperoxide as a function of time.

The present work was aimed at two objectives. In the first place, we would like to show that there is a difference in the second-order reaction in nematic and isotropic solvents; and, secondly to demonstrate a difference in the stereochemistry of the polyphenylacetylene polymer prepared in a nematic solvent and in an isotropic solvent.

If the collision step is the rate determining step in the polymerization, then the rates of polymerization in nematic and isotropic solvents are expected to differ. The stereochemistry of the polymerization can be followed by the conformation of the hydrogen atoms in relation to the phenyl groups in the polymer. The polymer unit of interest may be represented as



Infrared and nuclear magnetic resonance data for the trans-polymer, where X=5-10, are reported. The physical properties of the polymer are also reported which gives us all the measurements we need to characterize the products of the polymerization.

2. Attempted Polymerization of Some Vinyl Monomers.

The influence of the orientation of monomer molecules in media before polymerization is initiated has been studied for several acrylates. In all cases n-heptoxy-p-benzoic acid was used as the liquid crystalline media; it

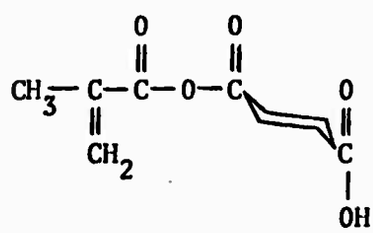
has a nematic phase from 96 to 144°C. The monomers studied in this project were: methacrylic acid, methyl methacrylate, n-octyl methacrylate.

Blumstein[1] found that there was no difference in the stereospecificity of polymers prepared in a liquid crystalline medium from a comparable one prepared in an isotropic media, if the polymerizations were carried to high conversions. With this result noted, all monomers were polymerized to high and low conversions to see if there was any difference.

The polymers were characterized by use of 100 Mc NMR spectroscopy. The tacticities were determined from spectra of poly(methyl methacrylate) in chloroform by the usual method of Bovey and Tiers[2].

Results and Discussion:

All the monomers were polymerized to high and low conversions at various ratios to the liquid crystalline media. With the exception of 1-methacryloyl-oxy-trans-cyclohexane-4-carboxylic acid,



all the results indicate there was no difference in the tacticity of the final polymer polymerized in either the liquid crystal or isotropic medium; in the case of the above monomer, only at low conversions was there any difference in tacticity. However, the difference was too small to be established with certainty as due to the liquid crystalline medium preorientating the monomer molecules. The above monomer was very difficult to polymerize in the liquid crystalline media, but it polymerized rapidly in the isotropic media.

At this point the contract terminated. These studies in liquid crystals

as reaction media show much promise for preparation of polymers with selected stereospecificity. It appears that selected molecular rearrangements can be modified in relationship to isotropic media when one uses liquid crystals as the solvent. Fundamental studies of the kinetics and mechanisms of reactions in liquid crystal media can be extensively explored and related to these reactions in isotropic solvents.

Liquid crystals as reaction media as explored for the first time under this contract should have an exciting future. Our research is continuing under Contract F44620-69-C-0021.

3. Polymerization of N,N-Dimethylacrylamide in Nematic Solvents.

The stereospecific polymerization of olefins to give highly crystalline tactic polymers has aroused great interest in similar types of polymers prepared from more polar monomers which contain atoms other than carbon and hydrogen. These stereospecific polymers have properties such as decreased solubility in organic solvents, and a much higher melting point than the corresponding random polymer. Such stereospecific polymerizations are accomplished by the use of anionic catalysts or Ziegler catalysts with isotropic solvents as benzene or toluene in the case of N,N-dimethylacrylamide[3]. This method of stereospecific polymerization provided a means for the preparation of a standard sample. Products prepared by the polymerization of N,N-dimethylacrylamide dissolved in nematic liquid crystal solvents will be compared to the standard sample by x-ray diffraction methods.

The objective in this work is the production of a stereospecific polymer of N,N-dimethylacrylamide by utilizing a nematic solvent containing molecules whose long axes are oriented in one direction. The molecules in a nematic solvent may be further oriented by the use of an electric or magnetic field

which could provide a matrix similar to a one-dimensional crystal for the polymerization to occur. This system could impose a special consideration forcing the second order reaction to give a stereospecific product.

We have prepared the stereospecific polymer of N,N-dimethylacrylamide utilizing n-butyllithium as catalyst and toluene as a solvent[3]. The poly(N,N-dimethyl)acrylamide is insoluble in benzene and has a softening point 290-300°. For comparison the following polymerizations of N,N-dimethylacrylamide utilizing different solvents and catalysts are shown in Table 4. The yields of random and stereospecific polymer are based upon the difference in solubility in benzene. Table 4 clearly indicates that thermal polymerization of N,N-dimethylacrylamide shown as No. 1 and a free radical polymerization, No. 2, yield random products. The nematic solvent used in all cases is di(p-methoxyphenyl)trans-cyclohexane-1,4-dicarboxylate. The use of this solvent along with lithium tert-butoxide as catalyst appears to give a good yield of stereospecific polymer as shown in Table 4, No. 4. The substitution of ethyl benzoate for the nematic solvent in the same reaction appears to change the conformation of the polymer from the stereospecific to the random polymer (see Table 4, No. 5). Ethyl benzoate is not a liquid crystal solvent and the selection as a solvent was based on the fact that it contains an ester linkage similar to the ester linkage in the nematic solvent. These preliminary results indicate the solvent may be exerting an influence but the final examination will be a comparison of the x-ray diffraction pattern of the random and stereospecific polymer[3].

REFERENCES

1. Blumstein, A., Kitagawa, N. and Blumstein, R., Molecular Crystals and Liquid Crystals 12, 215 (1971).

2. Bovey, F.A. and Teirs, G.V.D., J. Poly. Sci. 44, 173 (1960).

3. K. Butler, P.R. Thomas and G.J. Tyler, J. of Polymer Science 48, 357-366 (1960).

TABLE 4

Polymerization of N,N-Dimethylacrylamide

No.	Solvent	Catalyst	Reaction Temp.[b]	% Random Polymer.	% Stereo. Polymer.
1	Nematic	None	140-50°C	100	--
2	Nematic	Cumene Hydro Peroxide	140-50°	100	--
3	Nematic	LiOBu(t)	145°	70	30
4	Nematic	LiOBu(t)[a]	145°	15	85
5	Ethyl Benzoate	LiOBu(t)[b]	145°	100	--

[a] Catalyst added at three intervals.

[b] Reaction time in all cases 4-5 hours.

Mössbauer Studies

The concept of using the Mössbauer effect to study nuclear hyperfine interactions in liquid crystalline materials is new and as a result extreme care must be excercised in procuring the data. To our knowledge, the first data on this effect were taken under this contract. In this report we give the results of the preliminary studies of the Mössbauer effect in a smectic liquid crystal.

A careful calibration of the Mössbauer spectrometer (operating in the constant acceleration mode) was, therefore, accomplished by cross-checking spectra from several standard Mössbauer absorbers with each other and with published data. This, of course, was done after the spectrometer was constructed. Subsequent to the calibration, an oven and temperature control system suitable for study of liquid crystalline materials with the Mössbauer effect was designed, constructed and tested. Finally, it was decided to introduce Fe^{57} in the form of $FeCl_3$ into compounds having a smectic liquid crystalline phase, for two reasons:

(1) The knowledge that Fe^{57} is commonly accepted to be the best Mössbauer nucleus.

(2) The periodic layered structure of the smectic phase appears to be the most likely liquid crystalline phase to yield the recoil-free events necessary for the existence of the Mössbauer effect.

The above combination of $FeCl_3$ with liquid crystalline materials was effected in two ways: first, melting them together, and secondly, dissolving them both in a common solvent with the subsequent evaporation of the solvent. It was found that in several cases the presence of $FeCl_3$ destroyed the liquid crystal phase and in particular the smectic phase if its temperature range

was relatively small. However, by observing the Mössbauer effect in the above compounds the following qualitative information was obtained:

(1) The presence of a quadrupole split spectra (absent in pure $FeCl_3$) indicated that the iron (III) becomes intimately associated with the liquid crystalline molecule.

(2) The well resolved spectra show that the iron (III) occupies a unique position relative to the liquid crystal molecule.

Both of the above results strongly indicate that when the proper combination of smectic liquid crystal and $FeCl_3$ is found, the Mössbauer effect will prove to be a valuable tool in liquid crystal research.

After some preliminary studies this project was transferred to Contract No. F44620-69-C-0021 since finances were not available to carry it on the subject contract.

Structural Studies by Use of X-ray Methods

Crystallographic studies were carried out on the crystalline form of the nematogenic compound, 2,2'-dibromo-4,4'-bis(p-methoxybenzylidene amino) biphenyl. Several kinds of x-ray instrumentation were used to study this compound. X-ray photographs were taken using both precision and Weisenberg cameras and these photographs were used to establish cell dimensions for the crystal. These data are as follows:

$a = 7.631\text{Å} \pm 0.007$

$b = 11.548\text{Å} \pm 0.03$

$c = 15.990\text{Å} \pm 0.03$

$\alpha = 114.392° \pm 0.004$

$\beta = 105.584° \pm 0.002$

$\gamma = 92.156° \pm 0.004$

There are two molecules per cell. The space group is P1 or $P\bar{1}$ and there is no center of symmetry.

A Siemens Automatic Single Crystal Diffractometer was used to collect a complete set of nearly 5000 reflection intensities along the a-, b- and c-axes. These intensity data were corrected for Lorentz-polarization effects by the appropriate factors. The analysis of these data by the Patterson synthesis yielded the positions of the bromine atoms. These positions input into a first Fourier analysis yielded the positions of the carbon atoms in the biphenyl rings. A second Fourier analysis yielded the remaining non-hydrogen atoms. This crystal structure has been refined to an R value of 11.2%. We are continuing the refinement of these data in order to reduce the R value to less than 10%.

Absorption corrections and weights are to be applied and additional

refinement will be made using a block diagonal approximation necessitated by the size of the molecule and computer limitations. These steps will be followed by the final step of determining bond lengths, angles, etc.

Before closing this section it should be mentioned that we had hoped to do some low-angle x-ray scattering studies near the phase transitions, but after careful study it was decided that such studies would not be useful at this time. In order to interpret the continuous x-ray scattering at small angles, a general statistical theory of liquid crystals is needed. Since such a theory is non-existent at the present time, it has been decided to concentrate on the structure of smectic phases of liquid crystals. This study was transferred to Contract F44620-69-C-0021 when funds on the subject contract were exhausted. The studies on the smectic phases may be found in reports written under Contract F44620-69-C-0021.

Before this research was completed, funds were exhausted and the program was transferred to Contract F44620-69-C-0021. The complete structure analysis will be reported under that contract.

Conclusions

We feel we accomplished what we set out to do in this study, that is, expand our knowledge of the structure and properties of the liquid crystalline state of matter. From x-ray, Mössbauer and nmr studies, we now have a better knowledge of the structural characteristics of liquid crystalline systems. We have a better insight into the inelastic scattering characteristics of liquid crystals as well as an expanded knowledge of the deformation of polarized light by liquid crystalline systems.

In this report, we have pointed out areas of research which were initiated and carried out to a point where they were then transferred to Contract # F44620-69-C-0021 after funds on said contract were depleted. It did open up many new areas of research including Mössbauer measurements and a better insight into molecular configuration and ordering in liquid crystal media. We introduced the scientific community to the use of liquid crystals as solvents for the study of the kinetics and mechanisms of chemical reactions. These studies were related to identical reactions carried out in isotropic solvents. The synthetic program introduced new compounds exhibiting more than one nematic phase while other new compounds exhibited smectic phases which were first found under this project.

The scientific contributions from research carried on under this contract are quite significant and even though some of them were not completed while the contract was in effect, the research did reveal new findings which will be meaningful to our knowledge of the liquid crystalline state of matter.

Journal Publications Under This Contract

1. A. Saupe and J. Nehring, "On the Elastic Theory of Uniaxial Liquid Crystals", J. Chem. Phys. 54, 337 (1971).

2. N. Bravo, J.W. Doane, S.L. Arora and J.L. Fergason, "NMR Study of Molecular Configuration and Order in a Fluorinated-Liquid-Crystalline Schiff Base", J. Chem. Phys. 50, 1398 (1969).

3. T.R. Taylor, J.L. Fergason and S.L. Arora, "Biaxial Liquid Crystals", Phys. Rev. Lett. 24, 359 (1970).

4. S.L. Arora, T.R. Taylor and J.L. Fergason, "Polymorphism of Smectic Phases with Smectic A Morphology" in Liquid Crystals and Ordered Fluids, eds., J.F. Johnson and R.S. Porter, Plenum Press, New York, 1970, p. 321.

5. A. Saupe, "On Molecular Structure and Physical Properties of Thermotropic Liquid Crystals", Mol. Cryst. and Liq. Cryst. 7, 59 (1969).

6. S.L. Arora, T.R. Taylor and J.L. Fergason, "Mesomorphic Properties of Alkoxybenzylidene-aminoacetophenones", J. Org. Chem. 35, 1705 (1970).

7. W.E. Bacon and G.H. Brown, "Liquid Crystal Solvents as Reaction Media for the Claisen Rearrangement", Mol. Cryst. and Liq. Cryst. 6, 155 (1969).

8. W.E. Bacon and G.H. Brown, "Nematic Solvents as Media for the Claisen Rearrangement", Mol. Cryst. and Liq. Cryst. 12, 229 (1971).

9. S.L. Arora, J.L. Fergason and A. Saupe, "Two Liquid Crystal Phases with Nematic Morphology in Laterally Substituted Phenylenediamine Derivatives", Mol. Cryst and Liq. Cryst. 10, 243 (1970).

10. J.L. Fergason, S.L. Arora and T.R. Taylor, J. Org. Chem. 35, 4055 (1970).