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HOLOGRAPHIC RECORDING MATERIALS DEVELOPMENT

By C. M. Verber, R. E. Schwerzel,
P. J. Perry and R. A. Craig

Prepared under Contract No. NAS1-13834 by
BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

Research performed during the contract period has produced several significant advances in the development of organic photorefractive materials for application in a reversible holographic memory system. These studies have emphasized the evaluation of representative indigo and thioindigo derivatives and several stilbene derivatives, as well as a preliminary consideration of 15,16-dialkyldihydropyrene derivatives, and have led to the following achievements:

- The successful writing of phase holograms in a thioindigo/polymer gel system.
- The successful writing and erasing of phase holograms in a variety of indigo/polymer gel and indigo/solid polymer systems.
- The identification of indigoid dyes and 15,16-dialkyldihydropyrene derivatives as materials potentially suitable for utilization in an operational system.

The chemical research effort included photochemical studies of the stilbene, indigo, thioindigo, and dialkyldihydropyrene derivatives in solution and in a variety of polymer matrix materials, with the goal of optimizing the photorefractive behavior of the chemical system as a whole. A theoretical analysis has identified the spectroscopic properties required of optimal photorefractive materials, and has shown that both the indigoid dyes and the dialkyldihydropyrenes closely match the required properties.

The results achieved to date have demonstrated the possibility of using the photoisomerization of appropriate organic chemicals as the basis for a holographic recording system. The current status of the materials examined is discussed, and a brief summary of the research required to optimize the materials performance is presented.

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FOREWORD

This report was prepared by Battelle, Columbus Laboratories, under Contract No. NAS1-13834. This project has been monitored by Marvin Beatty, of The Flight Instrumentation Division, NASA-Langley Research Center. The program coordinator for the research was C. M. Verber, of Battelle's Solid State and Optical Sciences Section. Other contributors during the course of the period covered by this report were R. E. Schwerzel, P. J. Perry, R. A. Craig, C. M. Chapman, N. F. Hartman, R. G. Sinclair, and J. A. Hassell.

This report deals primarily with work performed during the contract period, March 23, 1975 to March 23, 1976. However, when required for clarification or completeness, the results of previous phases of this work have been included in this report.

SUMMARY

The research performed during this contract period has resulted in the successful writing and erasing of thick phase holograms in a variety of indigoid dyes, using several chemically different polymeric matrix materials. The diffraction efficiencies and writing sensitivities obtained to date are far from optimal; however, a theoretical analysis has identified the spectroscopic properties required to produce the change in refractive index required for a holographic memory material, and has shown that the low efficiencies obtained with the indigoid dyes are not inherent in the molecular structure of the compounds but result instead from matrix inhibition of the isomerization. Two other classes of materials, the fulgides and the 15,16-dialkyldihydropyrenes, were briefly examined and shown to have nearly optimal spectroscopic properties. These materials also undergo facile, reversible isomerization in polymer matrices, and can be cycled between the two isomers many times without degradation, although their rate of thermal back-reaction is too rapid at their present state of development. It is concluded that the development of an operational system based on the technology developed is feasible, although much research remains to be done.

BACKGROUND

The NASA high density memory program began in the late 1960's. At this time, Radiation Inc., a subsidiary of Harris Intertype, prepared a report for NASA/MSFC in which the block oriented random access memory (BORAM) system was described in detail. Shortly after this report was issued, the Battelle Columbus Laboratories were asked to consider possible approaches to securing a suitable holographic memory material for the BORAM. In this Background section the BORAM system will be briefly described. The memory material requirements which result from this system configuration will then be presented. The background to the present program will then be concluded with a brief summary of the results of Battelle's initial work for NASA/MSFC, performed under a subcontract to Radiation Inc., which indicated the advisability of undertaking the present program.

The BORAM System

The BORAM was designed with the long term goal of providing a flyable 10^{10} to 10^{12} bit read/write/erase memory system having no mechanically moving parts. The design proposed and ultimately brought to a preliminary brass-board stage by Harris Intertype utilized a holographic system to record a 128 x 128 bit pattern on a memory plane. A specific example of the system is shown schematically in Figure 1.

In addition to the lasers and beam handling optics, the system consists of an acoustooptic beam deflector, a block data composer or page composer, the memory plane or hologram array and the photodetector array. Data enters the memory serially at the block data composer which performs the dual functions of a buffer memory and an optical object whose hologram is recorded after the full bit pattern is entered. After the hologram is recorded, the block data composer is erased and a new bit pattern is entered and recorded on a new location in the memory plane. The memory plane location is selected by the acoustooptic beam deflector.

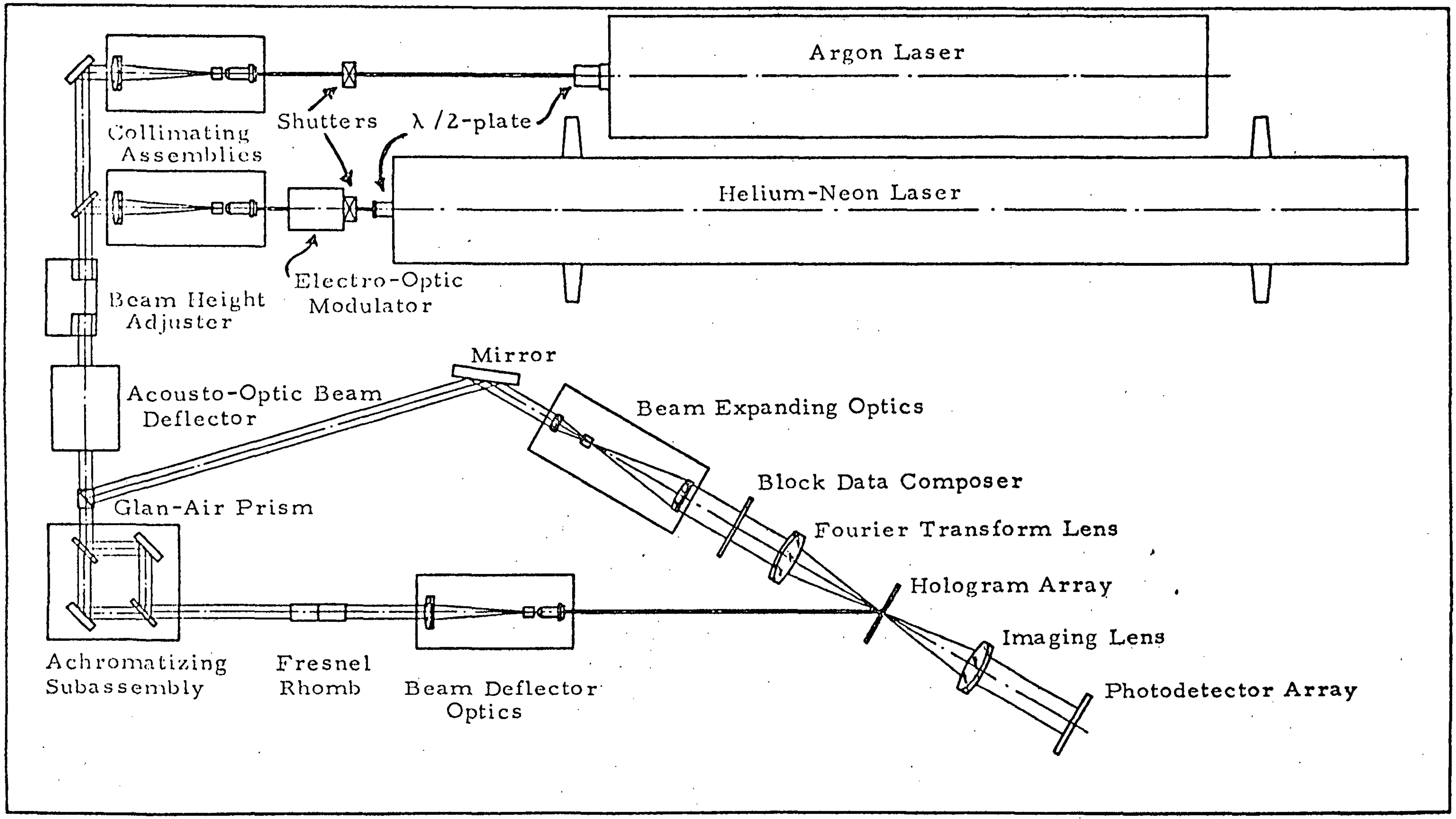


FIGURE 1. SCHEMATIC OF THE BLOCK ORIENTED RANDOM ACCESS MEMORY

In addition to spatially separating holograms by lateral displacement a large number of holograms may be recorded in the same volume of a thick recording medium. If these "spatially multiplexed" holograms are recorded using either different writing wavelengths or different angles between the signal and reference beams the individual holograms can be reconstructed separately. The original BORAM system called for recording the 128 x 128 bit page on a 1 mm^2 area of the recording plane. Superimposing 100 holograms and allowing some space between recording sites would lead to an average bit density of about 8×10^7 bits/cm^2. The memory plane would therefore have to have an area of 1.2×10^2 to 1.2×10^4 cm^2 or a linear dimension of 11 to 110 cm to allow 10^{10} to 10^{12} bits to be recorded.

The obvious impossibility of constructing an optical system capable of handling these larger dimensions, compounded by difficulties in implementing a spatial multiplex approach using sensitive read/write/erase materials and the lack of a suitable page composer, ultimately led to the abandonment of the no-moving-parts BORAM system. However, significant effort was made to develop a recording material for the BORAM before it was decided to investigate other memory concepts. The memory material requirements are discussed below.

Memory Material Requirements

The high capacity BORAM requires data storage in the form of thick phase-holograms. The thickness (~ 1 mm) is required for spatial multiplexing. Phase rather than absorption holograms are required in order to be able to attain reasonably efficient reconstruction of the holograms. In addition, the material must be capable of optical erasure, must allow a large number of write erase cycles without degradation, and must allow a large number of read operations with no loss of information. In addition to phase operation, reversibility and useful thickness of 1 mm, sensitivity and total available index change were taken as primary requirements for the recording material.

The sensitivity requirement was determined by assuming the availability of a suitable one-watt average-power laser for the recording process along with overall page composer and optical system losses of 95%. If, as was initially specified, 1000 holograms are written per second, 5×10^{-5} joules would be available at the surface of the recording material to write each 1 mm^2 hologram. For this hologram to have unit diffraction efficiency a change in index of refraction, Δn of about 10^{-4} is required. If sufficient signal is generated at the detector plane by a 1% efficient hologram, then a Δn of about 10^{-5} will suffice.

For multiple recording it is necessary that the material exhibit a linear response over the entire range of Δn required for recording all of the holograms. For 100 multiplexed holograms, we must therefore have $\Delta n_{max} \approx 10^{-3}$. The material research program was conducted with these goals in mind.

Utilization of Different Read and Write Wavelength

It was initially felt that the most favorable way to use either the cis-trans or the ferroelectric materials would be to read and write with different wavelengths. This mode of operation is desirable since reading with the write wavelength will produce unavoidable degradation of the hologram being read as well as degradation of the other spatially multiplexed holograms in the volume being interrogated. Also, reading at the write wavelength is an inherently lossy process since, in order to write efficiently, there must be a significant optical density at the write wavelength which will cause attenuation of the read beam. One of the initial goals in the cis-trans program was therefore to find materials in which there was a significant Δn exhibited outside the strong cis and trans absorption bands.

As the program progressed, it was realized that optical problems involved in reading and writing thick holograms at different wavelengths would probably result in a degraded image and would, at best, require a complete optical system and result in severe losses in diffraction efficiency(1). Recently one very clever way around this problem using two-photon excitation has been suggested(2) for use in $LiNbO_3$. It is not presently known whether a comparable scheme could be devised for a material exhibiting cis-trans isomerization. An alternative approach is, of course, to utilize much lower energies in reading than in writing. However, as stated earlier, this program was directed toward the situation in which two different wavelengths are employed.

Preliminary Conclusions

During the first Battelle program on Holographic Recording Materials, some 17 different material classes or recording phenomena were considered. The conclusion of this program was that there were "at least two classes of materials which satisfy all of the qualitative requirements and have the capability of satisfying all but one of the quantitative criteria. The material classes are the ferroelectric materials and the cis-trans isomers. Both of these material classes fail to meet the writing sensitivity criterion. In both we feel that continued work will bring the sensitivity to within a factor of ten of the desired value.

"Due to the fact that considerably more effort has been expended on the study of writing by optical damage in ferroelectrics than on the study of writing processes in cis-trans isomers, the state of the art of hologram formation in the former class of materials is at a much more advanced level. Consequently, it is recommended that immediate emphasis be placed on a continuation of the study of the cis-trans materials in an effort to locate, as soon as possible, any serious problems which have not been anticipated by the present work." It was in response to this recommendation that the present program was initiated.

PHOTOCHEMICAL cis-trans ISOMERIZATION

Basic Concepts

The fundamental process in a photochemical reaction is the absorption of light by the molecules of a chemical compound. When a molecule absorbs a photon of light, the molecule is promoted from its ground state (S_o) to a singlet excited state (S*) as indicated in Figure 2. This corresponds to a reorganization of the electronic structure of the molecule; that is, the arrangement of chemical bonds within the molecule is altered by the absorption of a photon. As a consequence of this, the electronically excited states of a molecule behave quite differently, both chemically and physically, from the ground state. The energy contributed by the photon may be dissipated in a variety of ways, some of which are shown in Figure 2.

It can be seen that S* may decay by emitting a photon (fluorescence), by transferring its energy as heat to its surroundings, or by undergoing a chemical transformation to become a different molecule. Alternately, S* may decay to another type of electronically excited state, known as a triplet excited state (T*), by the process of "intersystem crossing". The decay pathways available to T* parallel those available to S* quite closely, except that the emission of a photon from T* is referred to as phosphorescence rather than fluorescence. The triplet state differs from S* in three important ways:

- It is generally true that T* cannot be reached directly by the absorption of a photon; the photon promotes the molecule to S*, which can then decay to T*.
- The lifetime of T* is typically much longer (10^{-5} sec to 10 sec) than that of S* (10^{-10} sec to 10^{-6}); as a result, T* is much more prone to interactions with other molecules than is S*.
- By virtue of its longer lifetime and unique electronic structure, T* can undergo chemical reactions which are quite different from those characteristic of S*.

For any excited molecule the decay pathways shown in Figure 2 will be available. However, the relative probability of each pathway can vary

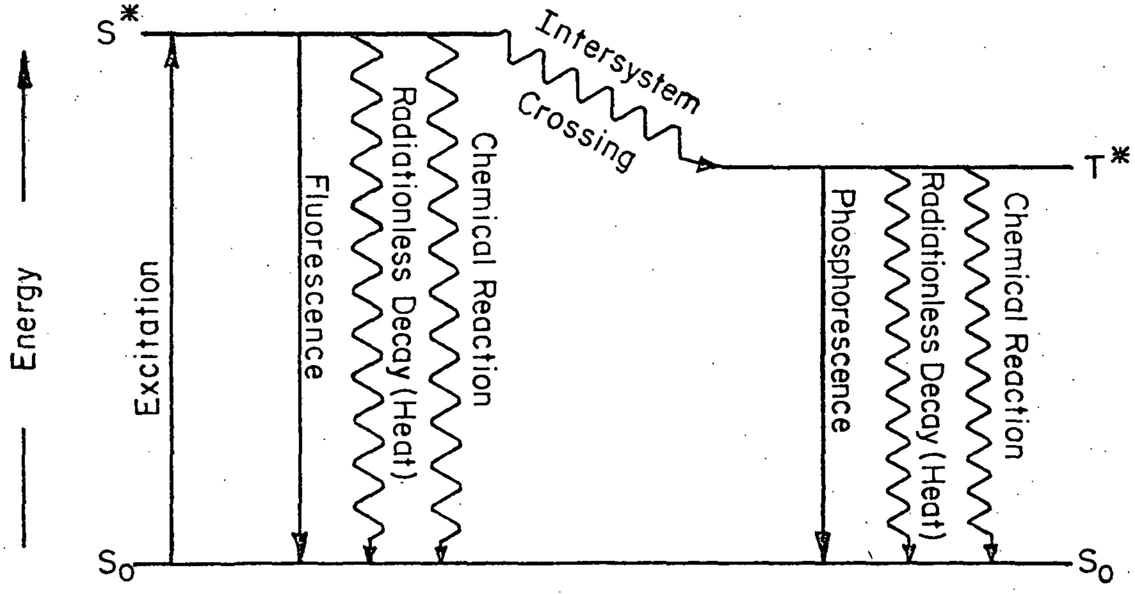


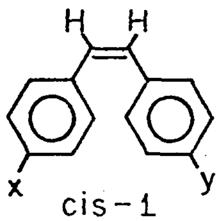
FIGURE 2. SCHEMATIC ILLUSTRATION OF PHOTOCHEMICAL EXCITATION AND DECAY PATHWAYS. RADIATIVE TRANSITIONS (INVOLVING THE ABSORPTION OR EMISSION OF A PHOTON) ARE INDICATED BY STRAIGHT ARROWS, RADIATIONLESS TRANSITIONS BY WAVY ARROWS. S_o, GROUND STATE; S*, SINGLET EXCITED STATE; T*, TRIPLET EXCITED STATE

considerably for chemically different molecules. As an example, some compounds (such as laser dyes) fluoresce very efficiently because fluorescence is the most probable decay pathway available from S*. Other compounds, which might have structures quite similar to the laser dyes, may fluoresce weakly or not at all because for them the probability of another decay pathway (for instance, intersystem crossing) exceeds that of fluorescence.

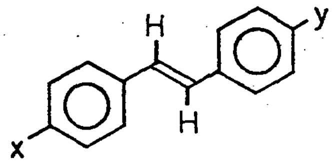
Direct *cis-trans* Photoisomerization

The above concepts may now be used to gain an understanding of the photochemical behavior of stilbenes indigos, and other materials which exhibit *cis*-*trans* photoisomerization. These compounds have been extensively studied by the research groups of G. S. Hammond, J. Saltiel, and G. M. Wyman in the United States, E. Fischer in Israel, and D. Schulte-Frohlinde in Germany, and much of the following discussion will be condensation of their results (3-6). While the following discussion is largely couched in term of the stilbenes, the concepts are common to most *cis*-*trans* materials.

Compounds of this type, such as the stilbenes (1), exist in two isomeric forms, which are referred to as *cis* and *trans* and which differ in the geometrical orientation of the phenyl groups with respect to the central double bond. Each isomer has its own set of singlet and triplet excited states. It is known that in *cis*-1 the two bulky phenyl groups are sufficiently close that the molecule must twist a bit in its ground state to keep the phenyl groups from bumping into one



cis-1



trans-1

X,Y = H, NO_2, OCH_3, NH_2, etc.

another. This has the effect of raising the ground state energy content of cis-1 relative to that of trans-1, as shown in Figure 3. In principle, the two isomers may be interconverted by a 180° twisting of the double bond. This requires that the bond be momentarily disrupted, and as a result a substantial amount of energy must be put into the molecule, either by the absorption of a photon or as heat, in order to carry out the isomerization. The thermal, or ground-state isomerization, which is promoted by heating the stilbene, proceeds only in the direction of cis→trans, since the trans isomer has the lower ground-state energy and is therefore the more stable of the two. This is represented in Figure 3 by the solid line connecting the trans and cis ground state levels. The large hump in the ground-state curve reflects the energy required to twist the double bond.

In contrast to the thermal process, the photochemical isomerization can be made to go either from cis to trans or from trans to cis, depending on the wavelength of light which is used. The cis isomer typically absorbs light of somewhat shorter wavelength than does the trans isomer, so it is possible to choose irradiation conditions under which either the cis-isomer or the trans-isomer absorbs most of the light. The separation between the cis and trans absorption maxima is not great (30-60 nm for most stilbenes) so laser excitation is particularly advantageous for this purpose. Since the isomer which absorbs the most light will preferentially undergo isomerization, it can be seen that for instance, a cis-rich photoequilibrium mixture can be obtained by irradiating at a wavelength where the trans-isomer absorbs strongly and the cis-isomer absorbs weakly.

Regardless of which isomer is irradiated, the initial act is the absorption of a photon to produce the singlet excited state of the isomer. This is represented by S*(t) and S*(c) in Figure 3. The evidence indicates that S*(t) and S*(c) then rapidly relax by a twisting motion to form an excited singlet state in which the stilbene is twisted by roughly 90 degrees. That is to say, the most stable geometry of the stilbene singlet excited state is a twisted stilbene, and this geometry is rapidly reached no matter which isomer was initially excited. This state has been dubbed the "phantom" singlet, as its presence cannot be confirmed by direct spectroscopic observation but is inferred from the results of a large number of experiments. It is

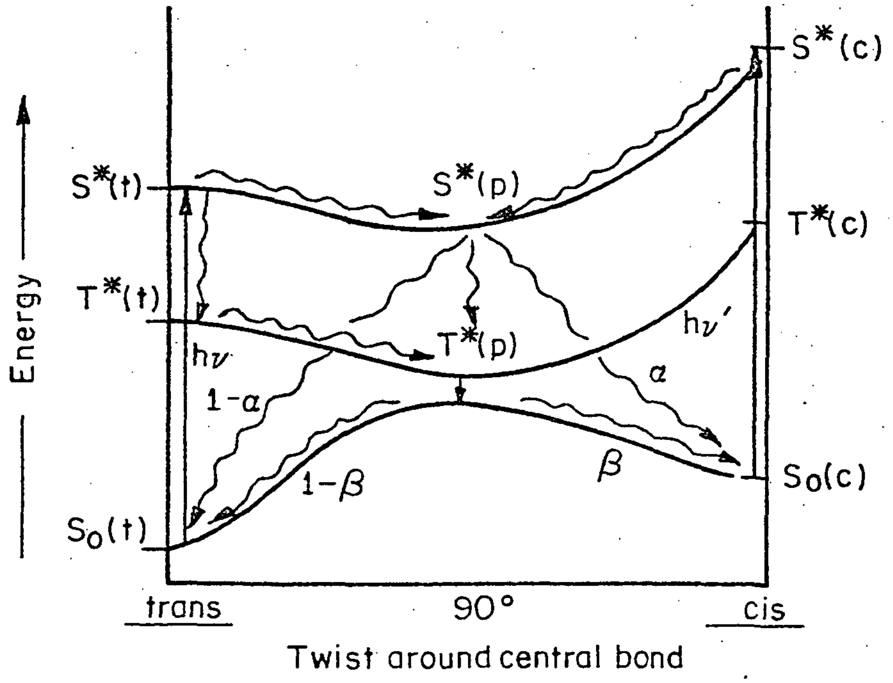
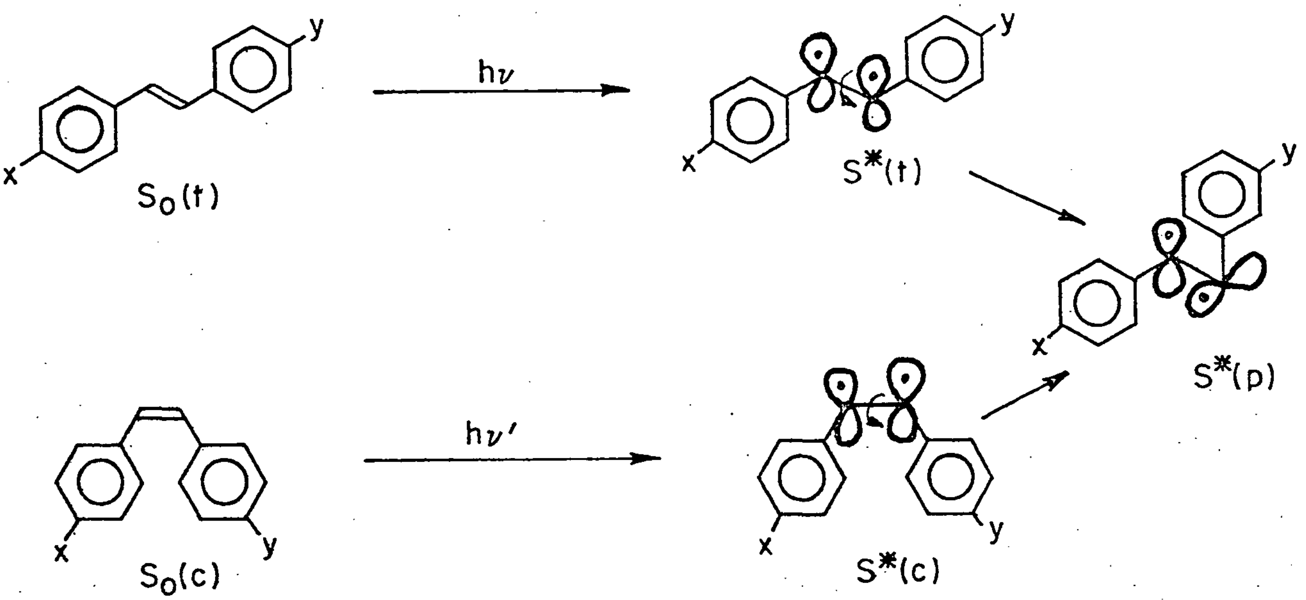


FIGURE 3. ENERGY-LEVEL DIAGRAM OF DIRECT *cis-trans* PHOTOISOMERIZATION

therefore labelled S*(p) in Figure 3, and may be visualized as shown below.



The electronic rearrangement involved in the transition from S_o to S* is manifested by the disruption of the central bond; this is the reason that twisting, and therefore isomerization, becomes quite facile in the excited state.

Depending on the nature of the substituents x and y, the twisted excited singlet may preferentially decay directly to the ground state with a probability (α) of forming cis and a probability ($1-\alpha$) of forming trans, or it may decay to a twisted triplet excited state, T*(p), having a geometry quite similar to that of S*(p). T*(p) can then decay to produce cis and trans ground state molecules with probabilities of β and ($1-\beta$), respectively. In terms of Figure 2, the pathway taken depends on the relative ease of intersystem crossing and of chemical reaction (isomerization) from the excited singlet. The key point is that both the singlet and triplet excited states have a common geometry which decays with a characteristic probability of forming the cis and trans ground states. In general, the decay ratio (cis/trans) of S*(p) will differ from that of T*(p), and both of these will vary depending on the nature of the substituents X and Y. There is some evidence that the trans singlet excited state, S*(t), is stable enough (for some stilbene derivatives) for intersystem crossing to a trans triplet, T*(t), to compete with formation of S*(p); this is indicated in Figure 3 by the wavy arrow from S*(t) to T*(t). In this case, T*(t) then quickly relaxes to form T*(p), the "phantom" triplet. The energy of T*(p) is very close to that of the twisted ground state, so T*(p) readily decays to the ground state and has an abnormally short lifetime ($< 10^{-6}$ sec). The formation of cis-rich or trans-rich photoequilibrium mixtures can be understood in the context of Figure 3 as the preferential "pumping" of one isomer, for instance, cis, with light of energy $h\nu'$. Thus, even though a fraction α (or β) of the cis isomer is returned to the ground state without change, this can be recycled by continued irradiation while the fraction $1-\alpha$ (or $1-\beta$) of trans continues to accumulate.

Photosensitized cis-trans Isomerization

Photochemical cis-trans isomerization may also be carried out by an indirect method known as photosensitization. In this technique, the compound is not irradiated directly, and therefore neither isomer absorbs light. Rather, another compound having carefully selected energy levels is added to the system and the wavelength of light is chosen such that this compound (the sensitizer), rather than the photoactive cis-trans material, will absorb the light. The energetics of sensitized isomerization are indicated in Figure 4. It is essential that the sensitizer have a relatively low-lying singlet excited state, S*(s), so that light of long wavelength can be used which will not be absorbed by the cis-trans compound (for instance, stilbene). The sensitizer must also have a high energy triplet state, T*(s), which lies above the stilbene triplet, and it must have a high efficiency of intersystem crossing so that

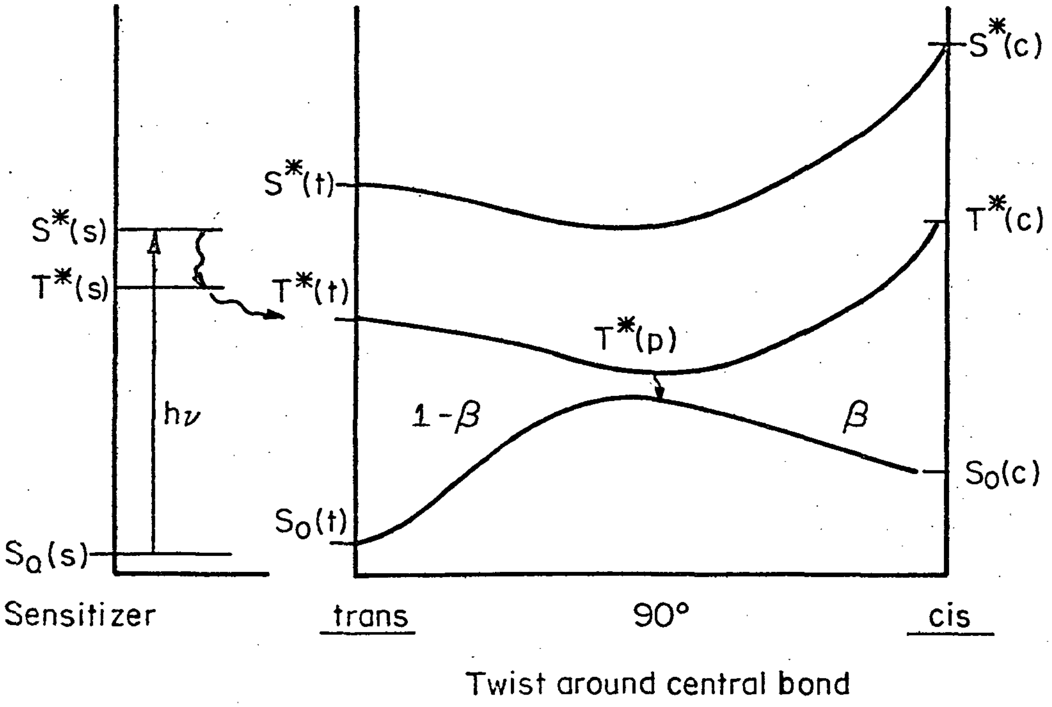


FIGURE 4. ENERGY-LEVEL DIAGRAM OF PHOTOSENSITIZED *cis*-*trans* ISOMERIZATION

T*(s) is readily formed. Given this situation, when a ground-state stilbene undergoes a collison with T*(s) there is a high probability that the energy of T*(s) will be transferred to the stilbene, promoting it directly to the triplet state. This is indicated for the formation of the trans-stilbene triplet state in Figure 4, but obviously the same process can occur with the cis-isomer. Because the energies of T*(t) and T*(c) are different, one may anticipate that the ease of energy transfer to the two isomers will differ, particularly when the sensitizer triplet energy lies between the energies of T*(t) and T*(c). This is in fact the case, and an elegant sort of "chemical spectroscopy" may be carried out by observing the effect on the photo-equilibrium mixture of using sensitizers with different triplet energies. Since energy transfer occurs much more readily when T*(s) lies several kcal above the stilbene triplet, as T*(s) falls below the energy of T*(c) energy transfer to T*(t) begins to dominate. Thus, selective "pumping" of the trans isomer can occur, and as Figure 5 (4) shows the amount of cis isomer in the photo-equilibrium mixture is enhanced enormously under these conditions. It should be kept in mind that the triplet state ultimately produced by photosensitized energy transfer is still the twisted stilbene triplet, T*(p), and that the decay ratio of this triplet is the same regardless of whether it is formed by direct excitation of one of the isomers or by energy transfer.

Energy Wastage and Side Reactions

Neither the direct nor the photosensitized isomerization of a cis-trans material is completely efficient and chemically clean. The greatest inefficiency is inherent in the isomerization process, in that a substantial fraction of the excited state decays back to the starting isomer with no net change. Some stilbene and indigo derivatives also fluoresce quite efficiently, and for them this constitutes another mode of energy wastage in direct photoisomerizations.

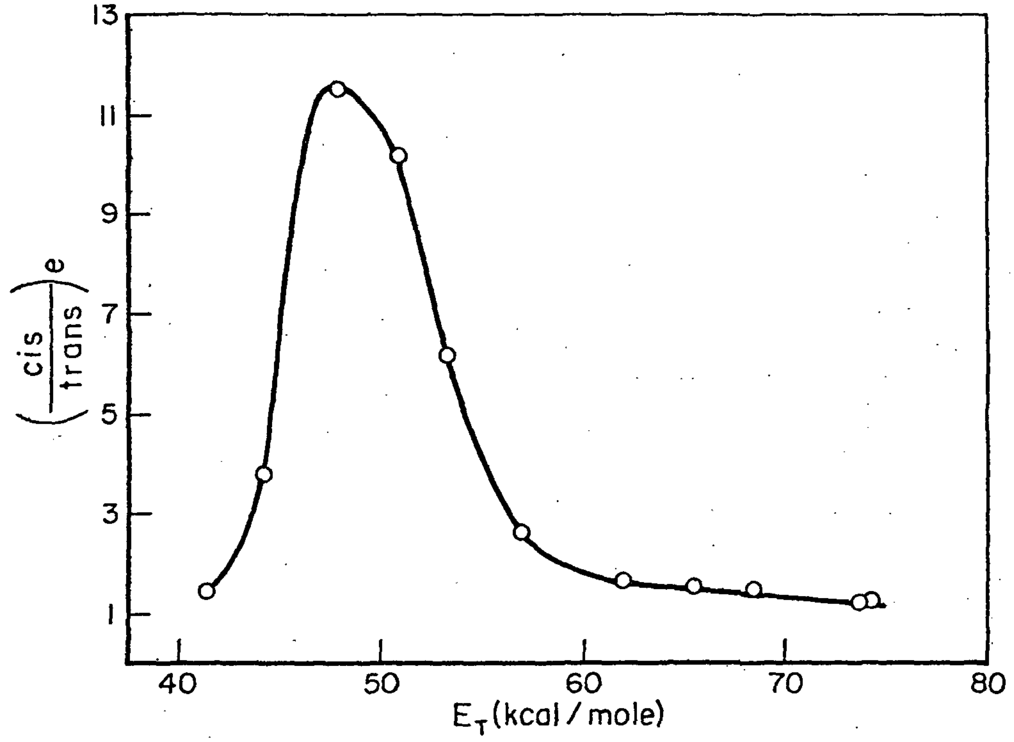
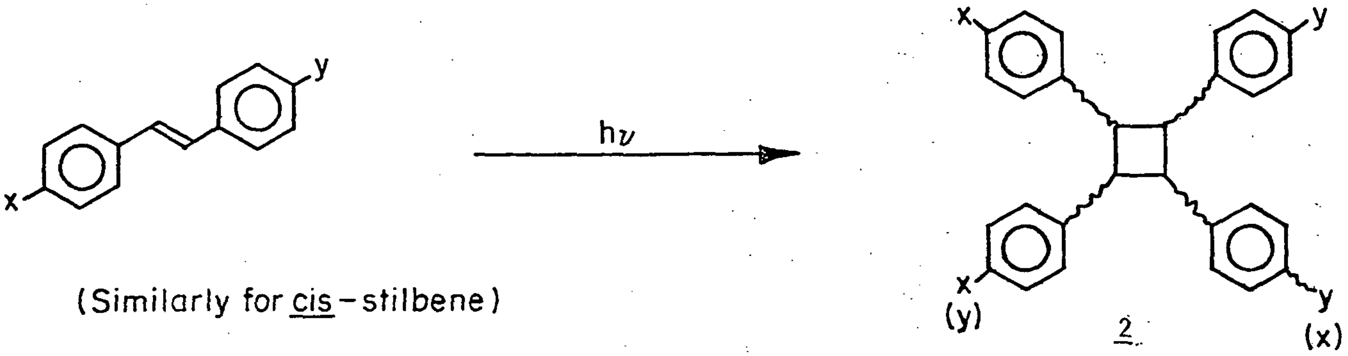


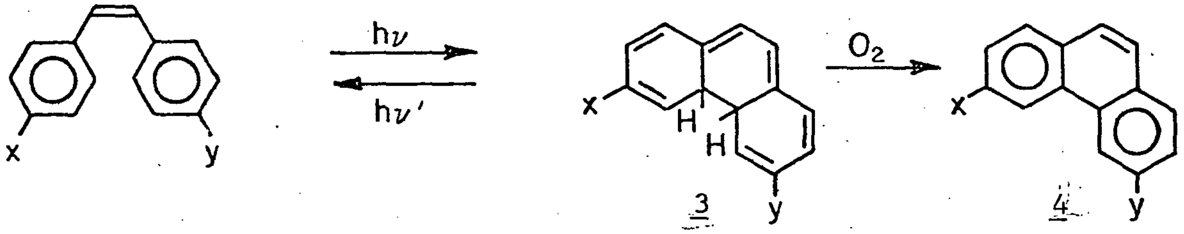
FIGURE 5. PHOTOEQUILIBRIUM cis/trans RATIOS FOR STILBENE AS A FUNCTION OF SENSITIZER TRIPLET ENERGY (FROM REFERENCE 4)

There are two side reactions, in addition to photoisomerization, which are particularly characteristic of stilbenes but not of indigo derivatives. These are photodimerization and photocyclization, as represented below. Photodimerization can occur with either <u>cis</u> or <u>trans</u> stilbenes, and typically produces a mixture of isomeric cyclobutane products (2) in which the various phenyl groups may either be <u>cis</u> or <u>trans</u> to each other. Photocyclization occurs only from the <u>cis</u>-isomer, and proceeds <u>via</u> the formation of an intermediate dihydrophenanthrene derivative (3). In the presence of air, 3 is irreversibly oxidized to the corresponding phenanthrene (4). The efficiencies of these reactions depend highly on the exact structure of the stilbene and on the irradiation conditions, although they are generally much less efficient than isomerization. Finally,

Photodimerization:



Photocylization:



the individual substituents x, y, etc, on a particular stilbene may undergo characteristic photochemical reactions of their own, such as hydrogen abstraction from solvent molecules. The importance of these reactions relative to isomerization must be evaluated individually for each compound. Because of these effects, a significant portion of the research effort expended in this program has been devoted to the development of a recording material (including both the photoactive compound and the polymer matrix to support it) which isomerizes efficiently with minimal degradation.

Matrix Considerations

While the occurrence of cis-trans photoisomerization in solution is well established, as indicated above, the adaptation of the reaction for holography requires that bulk diffusion of the molecules be restricted so as to retain the integrity of the hologram. A matrix system designed to allow recording of a reproducible image must be rigid and transparent, with the capacity for restricting migration of the photoactive material while allowing solvation of the compound and providing enough internal space or flexibility for the geometric change occurring in the isomerization process. Various concepts have been considered for the matrix during the course of this program, including

- Glass plate laminates
- Gels
- Microencapsulation
- Microvoids
- Bulk polymers
- Polymer-stilbene molecular engineering.

Glass Plates

The simplest concept would be use of two glass plates containing a film of solution. The glass would provide the structural integrity and confine the liquid. However, diffusion of the *cis-trans* material in the solution would still be a problem, and a thicker layer is required than could be obtained in this way. The diffusion might be limited, however, by using a high viscosity solution or even a gel.

Gels

A high viscosity solution would retard the diffusion of an image, but a better method might be to prevent the migration by using a gelled matrix. The gel is a three-dimensional solvent-swelled polymer system. The macrostructure of the gel traps the solvent, preventing it from migrating. If the gel structure is strong enough and the solvent "cells" (the solvent trapped areas between the gel structure) are tight enough, then the compound will be trapped in these cells and its diffusion will be restricted. Such a system could easily provide the desired resolution of 10^3 lines/mm since the entire molecular diameter (and therefore intramolecular space) of the high-molecular-weight polymers being considered falls well within the five micron dimension necessary.

Several techniques can be utilized to provide a non-aqueous gelled system. A gel can be made from a synthetic polymer by taking a long chain polymer and lightly crosslinking it. Ideally the polymer would be dissolved in a solvent containing the photoactive compound and then crosslinked; however, the crosslinking is a chemical reaction, which could cause chemical change in the recording compound. Another method for producing the gel would be to lightly crosslink the polymer and swell it to its maximum extent in a solvent containing the photoactive compound. Some of the solvent can then be pumped off, trapping the solvent and compound in the polymer.

Microencapsulation or Microvoids

Microencapsulation is the generation of small spheres which could be used to confine the stilbene solution by a rigid capsule wall. This method is ideal for providing a stable, nonmigrating system. However, the wall material must be matched so as not to interfere with the optical response. The microvoid is a matrix containing finite voids, like a foam, which are filled with the recording solution. Again the system must be designed to provide good optical properties.

Polymers

A solid, long-chain polymer would provide an ideal matrix material for the photoactive material (and sensitizers, if need be), allowing intermolecular spaces for the geometric conversion of the isomers. The polymer could then be formed into any desired shape, a film for instance. The greatest difficulty in this concept is that the polymer chains might prevent isomerization by sterically hindering the necessary twisting ring movement.

Polymer Molecular Engineering

The surest way of limiting the stilbene migration and preventing strong interaction with the polymer is through polymer molecular engineering in which stilbene molecules are chemically bonded onto a polymer chain. The bonding would be through a chemical reaction at a site on the stilbene which did not influence its efficiency for photoisomerization. An example of such a reaction as recently been reported by Mikés and his coworkers(3). This system has the obvious advantage of being single-phase, nonsolvent-based and self-contained. A polymer could be formed into any shape without the threat of loss of integrity, evaporation of solvent or migration of the image. However, such a system would require considerable development before it would be ready for use in the optical memory.

IMPLICATIONS OF THE RELATIONSHIP BETWEEN ABSORPTION SPECTRA AND INDEX CHANGE

Introduction

During the course of this project, theoretical investigations were initiated to establish the relationship between the absorption spectra of photoisomers and the index of refraction changes produced by their photoisomerization. Such a theoretical calculation is needed to provide a systematic guide to the choice of materials for phase-holographic storage systems. There are an enormous number of compounds which show a change of absorption spectrum under photoisomerization. Although an Edisonian approach is initially valuable to help establish the appropriate questions, a random testing of each of these compounds would be an enormous task and, in addition, would give no clue as to when the optimum selection had been obtained. On the other hand, the absorption spectra of many of these compounds are either known or theoretically predictable or easily measured. It would thus be extremely valuable to be able to infer from these absorption data the potential performance of the material for recording phase holograms.

For these purposes, it was assumed that the material in question has two absorbing isomers and that in the initial (trans) state the material is mainly composed of the isomer characterized by absorption at the longer wavelength. After irradiation at the writing wavelength, a fraction of these molecules are converted to the short wavelength absorbing (cis) state. The frequency spectra of all of the absorption bands are assumed to have a Lorentzian shape. With these assumptions, using the Kramers-Kronig relationships between the absorptive and refractive properties of a material, the change in index of refraction was studied as functions of the initial and final distribution of the two isomers, the locations of short and long wavelength bands and the width of these bands. Because these materials all have strong absorption bands at shorter wavelengths which are also shifted by the isomerization, the effects of these bands were also assessed.

Since the objective of the study has been the construction of thick phase holograms, three parameters were considered; these are the change in the index of refraction, the absorption (or optical density) in the final configuration and a figure of merit which is simply the ratio of these.

Qualitatively, the results are unsurprising. Remote, short wavelength bands were found to be unimportant. With all other parameters held equal, the further the cis absorption moves towards short wavelengths, the better the system will perform. Likewise, the sharper the original or shifted band or the longer the reading wavelength, the more efficient the system. In addition, a given fractional shift of population towards the short wavelength species is most effective the further the shift has progressed. That is, a shift from 60 percent to 90 percent cis isomer is more effective than the corresponding shift from 10 percent to 40 percent.

Kramers-Kronig Relationships

The response of a system to an applied field obeys one rule regardless of the nature of the applied field; this is that the response at a given time can depend only on field values at earlier times, i.e., causality is obeyed. This relatively simple observation turns out to permit some rather wideranging conclusions about the nature of the line or response function which connects the response to the applied field. In order to see how this comes about and in what way this helps in understanding the relationship between the optical constants, consider the electric polarization induced in a material by an applied electric field. Since the spatial variables do not affect the results they may be suppressed. The polarization is then,

$$P(t) = \int_{-\infty}^{\infty} K(t-t') \, E(t')dt' \quad . \tag{1}$$

If this equation is Fourier-transformed, it becomes

$$P(\omega) = \chi(\omega) \, E(\omega) = [\epsilon(\omega) - 1] \, E(\omega) \quad , \tag{2}$$

where $\chi(\omega)$, the dielectric susceptibility, is the Fourier transform of $K(t-t')$:

$$\chi(\omega) = \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} K(\tau) \quad . \tag{3}$$

As discussed, causality demands that the polarization at a time t must be independent of the applied fields for times t' later than t. Thus, $K(\tau)$ must vanish for $\tau < 0$; this requirement is reflected in the susceptibility by the corresponding requirement that $\chi(\omega)$ be analytic in the upper half plane. This, taken with the additional fact that $\epsilon - 1$ vanishes as $1/\omega^2$ for large frequencies leads to the conventional Kramer-Kronig relations between the real and imaginary parts of the dielectric response function.

$$\epsilon_2(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\omega'}{\omega' - \omega} \langle [1-\epsilon_1(\omega)] \rangle \quad , \tag{4a}$$

and

$$\epsilon_1(\omega) = 1 + \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\omega'}{\omega' - \omega} \epsilon_2(\omega) \quad . \tag{4b}$$

It can be shown also that ϵ has no zeroes in the upper half-plane; this can be demonstrated via an analysis of the integral

$$\frac{1}{2\pi i} \int_c d\omega \ln (\alpha(\omega) - a) \quad , \tag{5}$$

whose value is the difference between the number of poles and the number of zeroes of the function $\alpha(\omega) - a$ within the contour c(8). More simply however, it can be observed that $1/\epsilon(\omega)$ is itself the Fourier transform of a response function relating the charge density induced by an external test charge to the magnitude of the test charge. Consequently, $1/\epsilon$ must also be analytic in the upper half-plane. Thus, ϵ has neither zeroes nor poles in this plane.

The dielectric response function is related to the complex refractive index via

$$\epsilon = N^2 \tag{6}$$

where

$$N = n + ik$$

in which n and k are the conventional optical constants. As ϵ has no poles in the upper half plane, neither can N have poles there; likewise, as ϵ has no zeroes, N can have no branch points in this plane. Therefore, N is analytic in the upper half plane. Since N - 1 can also be shown to vary as ω^{-2} for large ω, then a pair of Kramers-Kronig relations exist between n and k

$$k = -\frac{1}{\pi} \int \frac{d\omega'}{\omega' - \omega} \, [n(\omega')-1] \quad , \tag{7a}$$

and

$$n(\omega) = 1 + \frac{1}{\pi} \int \frac{d\omega'}{\omega' - \omega} \, k(\omega) \quad . \tag{7b}$$

As can be seen, from these relationships, a complete knowledge of either n or k over the entire frequency range is sufficient to give the other quantity.

Theoretical Model of Recording Material

The index of refraction and extinction coefficient are related to the real and imaginary parts of the dielectric response function by

$$n = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1} \tag{7a}$$

and

$$k = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1} \tag{7b}$$

which follows directly from an inversion of $\epsilon = N^2$. It is the dielectric polarizability, $\chi = (\epsilon-1)/4\pi$ which is the fundamental physical variable and which will vary linearly with the density of various constitutents. In the approximation in which local field corrections are ignored the dielectric response function will also behave in this way. This would be a bad approximation for the physical situation under consideration, i.e., a dilute solution of molecules in a polymeric solvent as the solvent media itself has a substantial polarizability; thus we do not use this approximation. Provided that the observation conditions are such that the absorption of the host can be ignored (and this should be an excellent approximation as the host is transparent), the dielectric response can be written

$$\epsilon^2 = \epsilon_0 + 4\pi \left(\frac{\epsilon_0+2}{3}\right) \chi \quad , \tag{8}$$

where $\epsilon_0 = n_o^2$ is the dielectric response of the solvent and

$$\chi = N_c\chi_c + N_t\chi_t \quad , \tag{9a}$$

is the complex polarizability of the diluent molecules. Here χ_c and χ_t are the (molar) polarizability of the cis and trans isomers respectively, and N_c and N_t are the respective concentrations. If it is assumed that the total number of diluent molecules is fixed at N and the isomeric fractions are f_c and f_t respectively then

$$\chi = N(f_c\chi_c + f_t\chi_t) \quad . \tag{9b}$$

For the purpose of describing the behavior of a mixture of atoms as used in a photorefractive mode, it is desirable to establish an appropriate figure of merit. A reasonable choice for such a figure of merit might be the ratio of the change in the index of refraction to the absorption in the final--or "read"--state, i.e.,

$$M = \frac{|\Delta n|}{\frac{2\omega}{c} k_{\text{final}}} \quad , \tag{10}$$

as the absorption for any system characterized by an extinction coefficient k is given by $\frac{2\omega}{c}k$.

This figure of merit will indicate the relative ease with which information stored photochemically can be recovered by an optical reading process. This is reasonable as the larger the change in the index of refraction, the more distinct the information will appear and the larger the absorption at the reading frequency, the more difficult the read operation will become (and the greater the likelihood that the reading operation will destroy the written information).

If we write the dielectric response as the sum of the host response plus a correction term

$$\epsilon_1 = \epsilon_0 + \Delta_1 \tag{11a}$$

and

$$\epsilon_2 = \Delta_2 \tag{11b}$$

and assume Δ_1 and Δ_2 to be much smaller than ϵ_0 (this is always an excellent approximation as the solubility limits for the diluents in rigid matrices are extremely small), then, to first order in small quantities the optical parameters are

$$n = n_0 + \frac{\Delta_1}{2n_0} \tag{12a}$$

and

$$k = \frac{\Delta_2}{2n_0} \tag{12b}$$

where $n_0 = \epsilon_0^{1/2}$. Under these conditions,

$$n = n_0 + N_c\,\delta n_c + N_t\,\delta n_t \tag{13a}$$

and

$$k = N_c k_c + N_t k_t \tag{13b}$$

in which δn_c and δn_t are the molar indices of refraction of the cis and trans isomers respectively and k_c and k_t are their extinction coefficients. Here δn_c and k_c are respectively

$$\frac{2\pi}{3}\left(\frac{n_0^2 + 2}{n_0}\right) \chi_1^c \quad ,$$

and

$$\frac{2\pi}{3}\left(\frac{n_0^2 + 2}{n_0}\right) \chi_2^c$$

from Equations 8 and 9 with similar relations for these parameters for the trans molecules. Thus, the change in refractive index induced by converting trans isomers to the cis form is

$$\Delta n = N \, \Delta f \, (\delta n_c - \delta n_t) \quad , \tag{14a}$$

where conservation of the total number of diluent molecules has been invoked. Here Δf is the change in the fraction of the molecues in the cis isomeric state. Note that if, δn_c is less than δn_t as will most often be the case, this leads to a decrease in the index of refraction, i.e., Δn is negative. Under these conditions, the figure of merit becomes

$$M = \frac{\Delta f \, (\delta n_t - \delta n_c)}{\frac{2\omega}{c} \left[(f_c^0 + \Delta f) k_c + (f_t^0 - \Delta f) \, k_t \right]}$$

$$= \frac{\Delta f \, (\delta n_c - \delta n_t)}{\frac{2\omega}{c} \left[(f_c^0 + \Delta f) k_c + (1 - f_c^0 - \Delta f) k_t \right]} \quad . \tag{14b}$$

In order to proceed, and to estimate the effects of variations in material properties upon the figure of merit, it is useful to construct a model lineshape for the diluent molecules. An appealing choice, on physical grounds, is the Lorentzian lineshape.

$$k = A \, \frac{\omega \, \Gamma^2}{(\omega_0^2 - \omega^2)^2 + \omega^2 \, \Gamma^2} \tag{15a}$$

which has the additional attraction that its Kramers-Kronig inversion is analytic

$$\delta n = A \; \frac{\Gamma(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2} \quad . \tag{15b}$$

Here A is a constant to be determined by experiment, ω_0 is the resonant frequency and Γ the width at half-maximum. If the absorbing diluent has more than one interesting resonant frequency, this factor can easily be accommodated by a summation over the resonances, viz.

$$k = \sum_j A_j \frac{\omega \Gamma_j^2}{(\omega_{0j}^2 - \omega^2)^2 + \omega^2\Gamma_j^2} \quad . \tag{16b}$$

For the moment, however, only the case of a single isolated resonance shall be considered.

In order to fit 15a or 16a to experiment, information on the absorption of the material in question is needed. Absorption measurements often are tied to a base of ten, i.e.,

$$I = I_0 \; 10^{-\epsilon N \ell} \tag{17}$$

where I is the final intensity, I_0 the initial, N the molar concentration of the absorber, ℓ the path length and ϵ the molar extinction coefficient. On the other hand, the intensity variation is related to the extinction coefficient by

$$\frac{1}{I}\frac{dI}{d\ell} = \frac{-2\omega}{c} k \tag{18}$$

or

$$\epsilon\ell = 2\,\frac{\omega}{c}\,\frac{k}{N \ln 10}$$

$$= \frac{2}{cN\ln 10}\,A\,\frac{\omega^2\Gamma^2}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2} \tag{19}$$

which gives,

$$A = \varepsilon_{max} \frac{cN \ln 10}{2} \quad . \tag{20}$$

Using this, and converting the expressions for the optical parameters from frequency to wavelength and adjusting for unit concentration, these become

$$\delta n = \frac{\ln 10 \, \varepsilon_{max}}{8\pi^2 c} \frac{\Gamma \lambda_0^2 \lambda^2 (\lambda^2 - \lambda_0^2)}{[(\lambda^2 - \lambda_0^2)^2 + \lambda^2 \lambda_0^4 \Gamma^2 / 4\pi^2 c^2]} \quad , \tag{21a}$$

and

$$k = \frac{\ln 10 \, \varepsilon_{max}}{16 \pi^3 c^2} \frac{\lambda^3 \lambda_0^4 \Gamma^2}{[(\lambda_0^2 - \lambda^2)^2 + \lambda^2 \lambda_0^4 \Gamma^2 / 4\pi^2 c^2]} \quad . \tag{21b}$$

It is desired to use these expressions to analyze the behavior of the figure of merit M when a fraction of the molecules is transferred from the one isomeric state to the other. For the these purposes, a useful but not necessary approximation is to assume that the oscillator strengths of the two isomeric forms are identical. This is actually a good approximation and simply states that, in the isomeric transition, although the height, width and location of the absorption band may change, it does not break up into a number of isolated bands, i.e., the f-sum (Thomas-Reich-Kuhn) rule (for the electrons involved) is exhausted by the single band. This says

$$\int \omega \, \mathrm{Im}\, \epsilon(\omega) \, d\omega = \frac{2\pi^2 e^2 N_e}{m} \quad ,$$

where (e) and (m) are the charge and mass on the electron respectively, and N_e is the number of electrons involved in the absorption structure. When applied to the Lorentzian structure Equation 15a, the requirement that the oscillator strength remain unchanged during the cis-trans transition thus becomes

$$\int \varepsilon(\omega) \, d\omega = \text{unchanged} \tag{22a}$$

or equivalently the product

$$A \, \Gamma = \text{unchanged} \tag{22b}$$

The quantity (Γ) is the width at half maximum when the excitation coefficient is viewed as a function of the angular frequency ω; if the wavelength is chosen to be the independent variable, the corresponding width at half maximum is given by

$$\Delta = \frac{\lambda_0^{\,2}\,\Gamma}{2\pi c} \quad . \tag{23}$$

Thus, by (22b) the product

$$\frac{A\Delta}{\lambda_0^{\,2}} \quad \text{or} \quad \frac{\varepsilon_{\max}\Delta}{\lambda_0^{\,2}} \quad , \tag{24}$$

should remain unchanged in a <u>cis-trans</u> isomeric transition in which the electronic structure is only moderately perturbed. If equations 21 are used in the expression for the figure of merit and the above relationships between strengths of cis and trans absorptions incorporated, this becomes

$$M = \frac{\dfrac{\Delta f\,(\lambda_0^{c2} - \lambda^2)}{\Delta^c\,(f_0^{\,c} + \Delta f)\,4\pi}\left[\,1 - \left(\dfrac{\lambda_0^{\,t}}{\lambda_0^{\,c}}\right)^2 \dfrac{(\lambda^2 - \lambda_0^{t2})}{(\lambda^2 - \lambda_0^{c2})}\,\dfrac{D_c}{D_t}\,\right]}{\left[1 + \left(\dfrac{1}{f_0^{\,c} + \Delta f} - 1\right)\left(\dfrac{\lambda_0^{\,t}}{\lambda_0^{\,c}}\right)^2 \dfrac{\Delta^t}{\Delta_c}\,\dfrac{D_c}{D_t}\,\right]} \quad , \tag{25}$$

where

$$D = (\lambda^2 - \lambda_0^{\,2})^2 + \lambda^2\,\Delta^2 \quad .$$

Likewise, the change in index of refraction induced by the change in isomeric fractions of the diluent molecules is

$$\Delta n = \frac{\varepsilon^c_{\max}\,\Delta^c\,\ell n\,10\,\Delta f \lambda^2\,(\lambda^2 - \lambda_0^{c2})}{4\pi\,D_c}\left[\,1 - \left(\frac{\lambda_0^{\,t}}{\lambda_0^{\,c}}\right)^2 \left(\frac{(\lambda^2 - \lambda_0^{t2})}{(\lambda^2 - \lambda_0^{c2})}\right)\frac{D_c}{D_t}\right] \tag{26}$$

The preceding discussion has related to the effects on the photochromic properties brought about by a single absorption band. Actual materials will also have deeper lying electronic levels which will give rise to absorption bands at shorter wavelengths. In order to assess the contributions due to these, it is assumed that there is but a single additional band so that the optical parameters become

$$k = A_1 \frac{\omega \Gamma_1^2}{(\omega_{01}^2 - \omega^2)^2 + \omega^2 \Gamma_1^2} + A_2 \frac{\omega \Gamma_2^2}{(\omega_{02}^2 - \omega^2)^2 + \omega^2 \Gamma_2^2} \quad , \tag{27a}$$

and

$$\delta n = A_1 \frac{\Gamma_1 (\omega_{01}^2 - \omega^2)}{(\omega_{01}^2 - \omega^2)^2 + \omega^2 \Gamma_1^2} + A_2 \frac{\Gamma_2 (\omega_{02}^2 - \omega^2)}{(\omega_{02}^2 - \omega^2)^2 + \omega^2 \Gamma_2^2} \quad , \tag{27b}$$

from Equation 16.

Alternatively, if these parameters are expressed as functions of wavelength they become

$$\delta n = \frac{\ln 10}{8\pi^2 c} \left\{ \frac{\epsilon_{1\,\max} \Gamma_1 \lambda_{01}^2 \lambda^2 (\lambda^2 - \lambda_{01}^2)}{(\lambda^2 - \lambda_{01}^2)^2 + \frac{\lambda^2 \lambda_{01}^4 \Gamma_1^2}{4\pi^2 c^2}} + \frac{\epsilon_{2\,\max} \Gamma_2 \lambda_{02}^2 \lambda^2 (\lambda^2 - \lambda_{02}^2)}{(\lambda^2 - \lambda_{02}^2)^2 + \frac{\lambda^2 \lambda_{02}^4 \Gamma_2^2}{4\pi^2 c^2}} \right\} \tag{27c}$$

and

$$k = \frac{\ln 10}{16\pi^3 c^2} \left\{ \frac{\epsilon_{1\,\max} \lambda^3 \lambda_{01}^4 \Gamma_1^2}{[(\lambda_{01}^2 - \lambda^2)^2 + \frac{\lambda^2 \lambda_{01}^4 \Gamma_1^2}{4\pi^2 c^2}]} + \frac{\epsilon_{2\,\max} \lambda^3 \lambda_{02}^4 \Gamma_2^2}{[(\lambda_{02}^2 - \lambda^2)^2 + \frac{\lambda^2 \lambda_{02}^4 \Gamma_2^2}{4\pi^2 c^2}]} \right\} \tag{27d}$$

In Equations 27, the various parameters all have the same meanings as ascribed to them earlier with the exception that the subscripts (1) and (2) refer to the longer and shorter wavelength peaks respectively. Under the same assumptions as were applied earlier, i.e., that under the isomerization the number of electrons associated with each band does not change, then condition 24 will hold separately for each band. That is

$$\frac{\epsilon_{max}\,\Delta}{\lambda_0^2}\ (\text{with } \Delta = \lambda_0^2\ \Gamma/2\pi c)$$

will be a constant for each band separately.

The determination of the effect of the isomerization upon the index of refraction and upon the figure of merit is straightforward but somewhat tedious. The results are sufficiently complicated that little is to be gained by writing them down explicitly. Instead the effects due to these bands will be displayed in the accompanying figures.

Results

For the purposes of attempting to understand the dependence of the index of refraction and the figure of merit upon the parameters of the material, it will be assumed that these values initially are:

λ_t° = 530 nm

ϵ_{max}^t = 7000

Δ_t= 70 nm

in the trans isomeric form and:

λ_c° = 450 nm

ϵ_{max}^c = 4000

Δ_c= 82 nm (derived)

in the cis isomeric form. These values were chosen as representative of materials under consideration.

In Figures 6-8, $(-\Delta n)$ and M are displayed as a function of the reading wavelength. In Figures 6 and 7 it is assumed that initially 90 percent of the diluent is in the trans isomeric state and that, in the final configuration, 10 percent is in that state. In Figure 6, the position of the cis peak λ_0^c is allowed to vary while in Figure 7 the width of this peak, Δ^c is varied. In Figure 8, all the physical parameters are fixed at the representative value and the fractional isomeric change is fixed at .3, however, the final concentration of the cis-isomer was allowed to take on the values of.3, .5 and .9. Finally, in Figure 9, the effects of a core band in the UV on Δn and M are displayed. In this figure, the above parameters are used for the near bands; it was assumed that there was one pair of short wavelength bands with the same weight as the near bands and their wavelength is .45 that of the near bands; Δn and M are shown in the absence of the UV bands, and with UV bands with widths of .1 and .45 those of the near bands.

These results are, as discussed in the introduction, neither unexpected nor surprising. In Figure 6, it is seen that as the final state (cis) peak moves further into the UV, both the change in the index of refraction and the figure of merit improve. This is quite reasonable for, as the cis peak moves into the UV, δn_c at the reading wavelength is reduced and the difference $\delta n_c - \delta n_t$ increased; from Equation 14a this leads to an increased change in the magnitude of Δn as observed. At the same time, the absorption in the final state decreases somewhat as the cis-peak moves into the UV because this peak contributes to this absorption. In Figure 7, it is seen that as the cis peak becomes narrower, the change in the magnitude of the index of refraction change decreases by a small amount but the figure of merit improves considerably. These results also are not surprising; for remote bands of equal strength, δn_c will be slightly smaller at the reading wavelength for a broad band than for a narrow band. Thus the small increases in the magnitude of Δn. However, the absorption associated with this remote band is going to be much smaller for the narrower band than for the broader. Thus, over the range of values considered, the effect on the final state absorption dominates in the figure of merit.

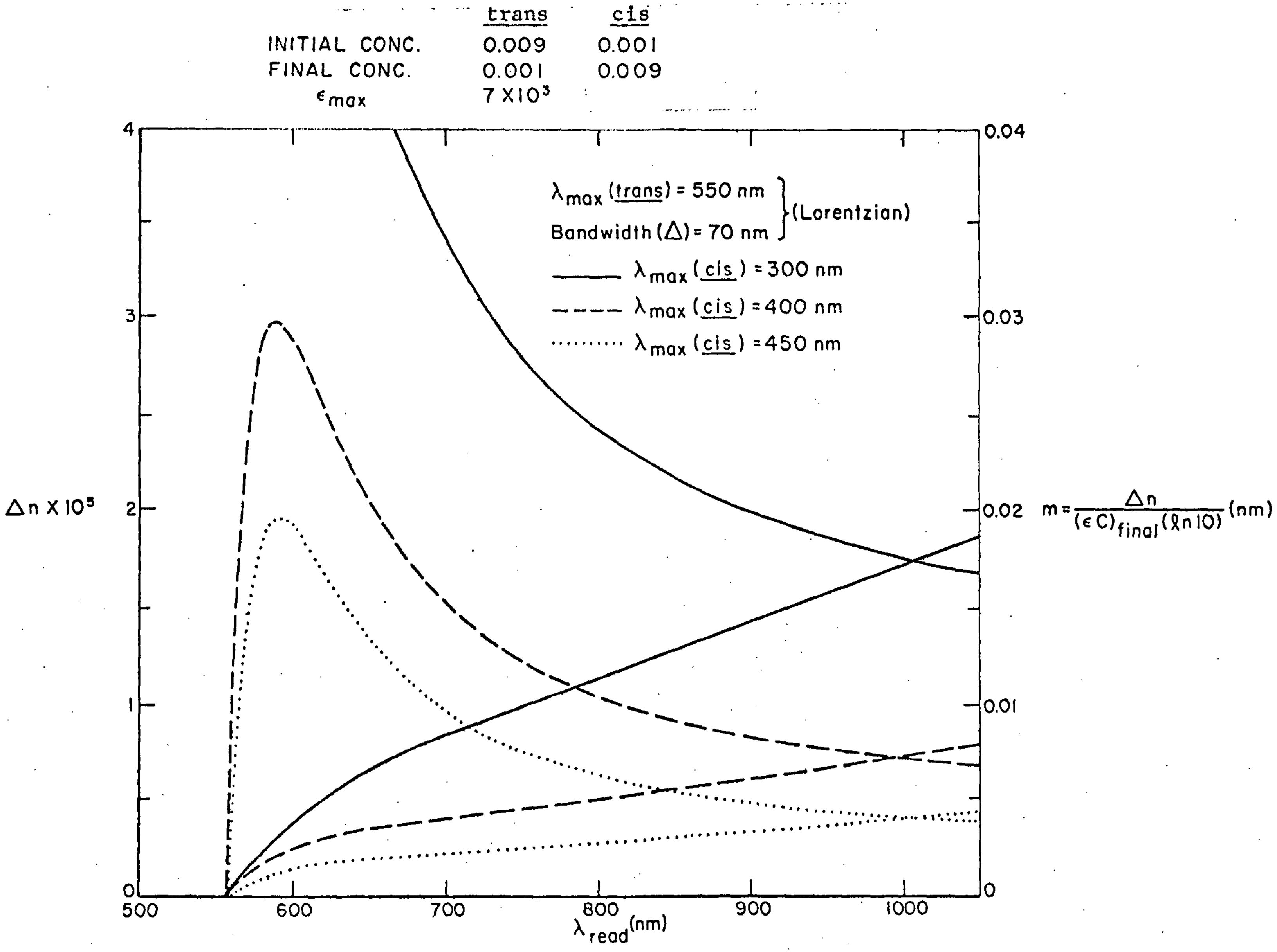


FIGURE 6. CHANGE IN INDEX OF REFRACTION AND FIGURE OF MERIT AS A FUNCTION OF READING WAVELENGTH FOR SEVERAL VALUES OF THE POSITION OF THE <u>cis</u> PEAK. ALL OTHER PARAMETERS ARE HELD CONSTANT

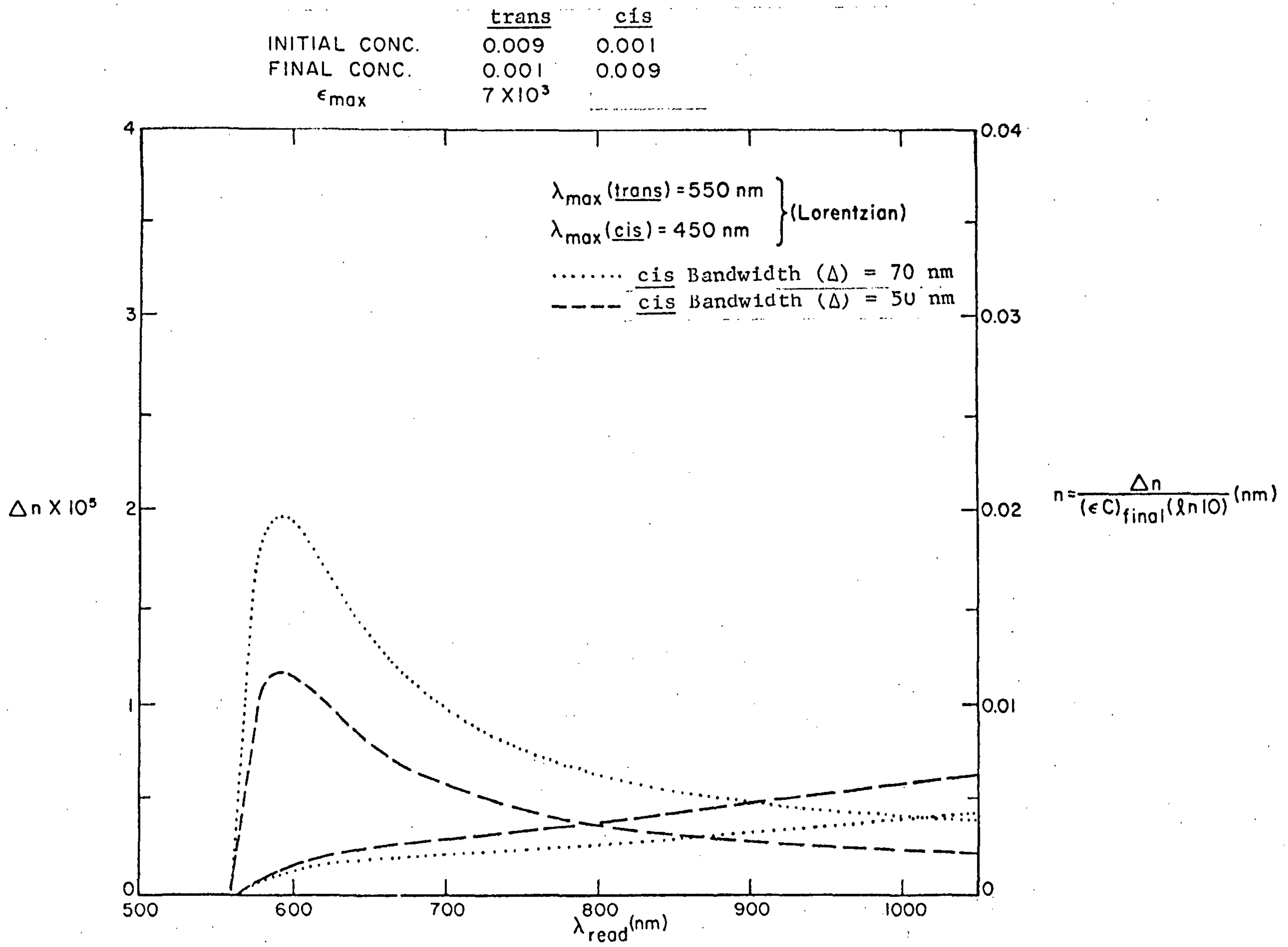


FIGURE 7. CHANGE IN INDEX OF REFRACTION AND FIGURE OF MERIT AS A FUNCTION OF READING WAVELENGTH FOR SEVERAL VALUES OF THE WIDTH OF THE cis PEAK. ALL OTHER PARAMETERS ARE HELD CONSTANT.

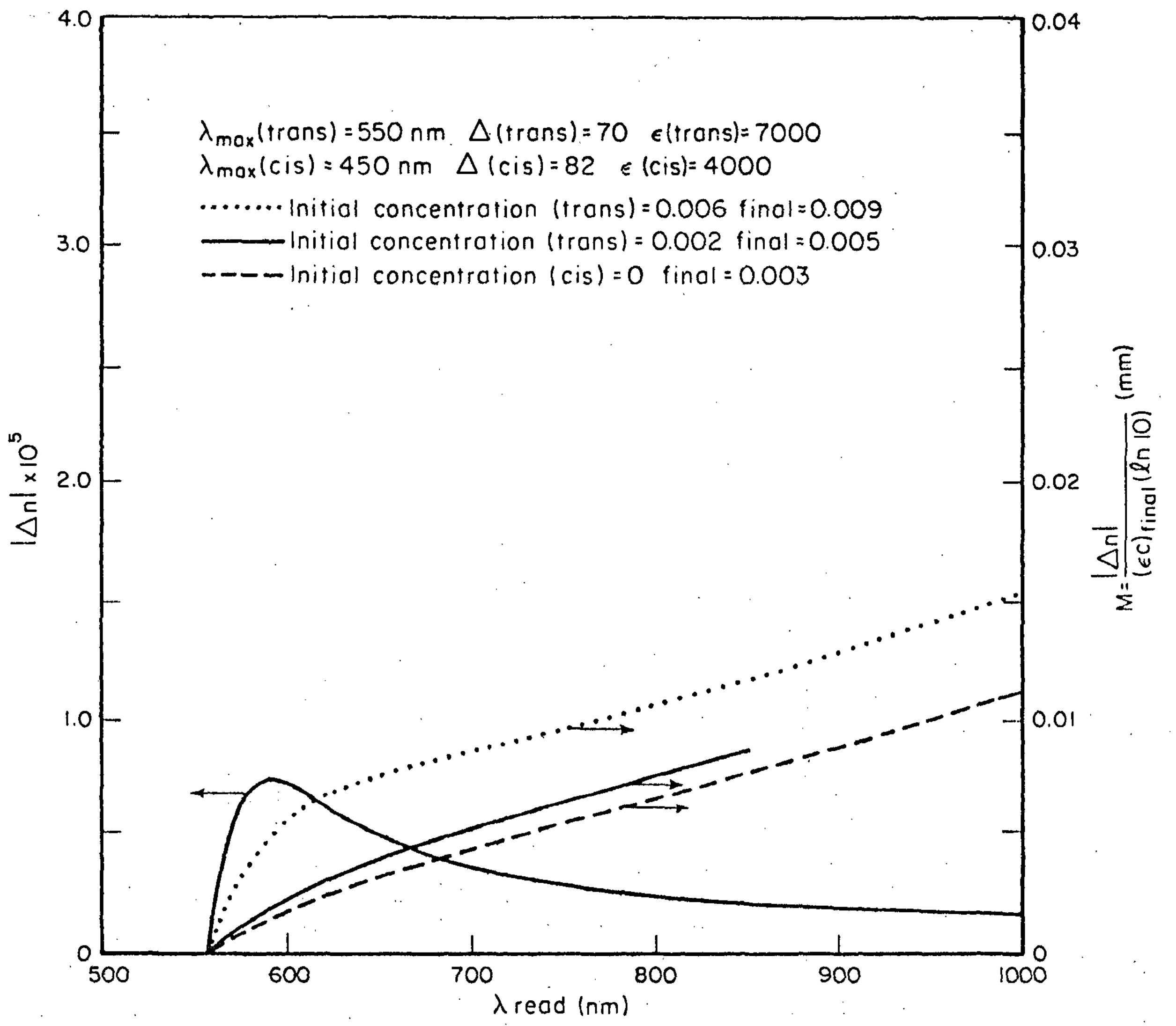


FIGURE 8. CHANGE IN INDEX OF REFRACTION AND FIGURE OF MERIT AS A FUNCTION OF READING WAVELENGTH FOR AN IOSMERIZATION QUANTUM YIELD OF .3 AND FOR SEVERAL VALUES OF THE FINAL CONCENTRATION OF THE cis ISOMER

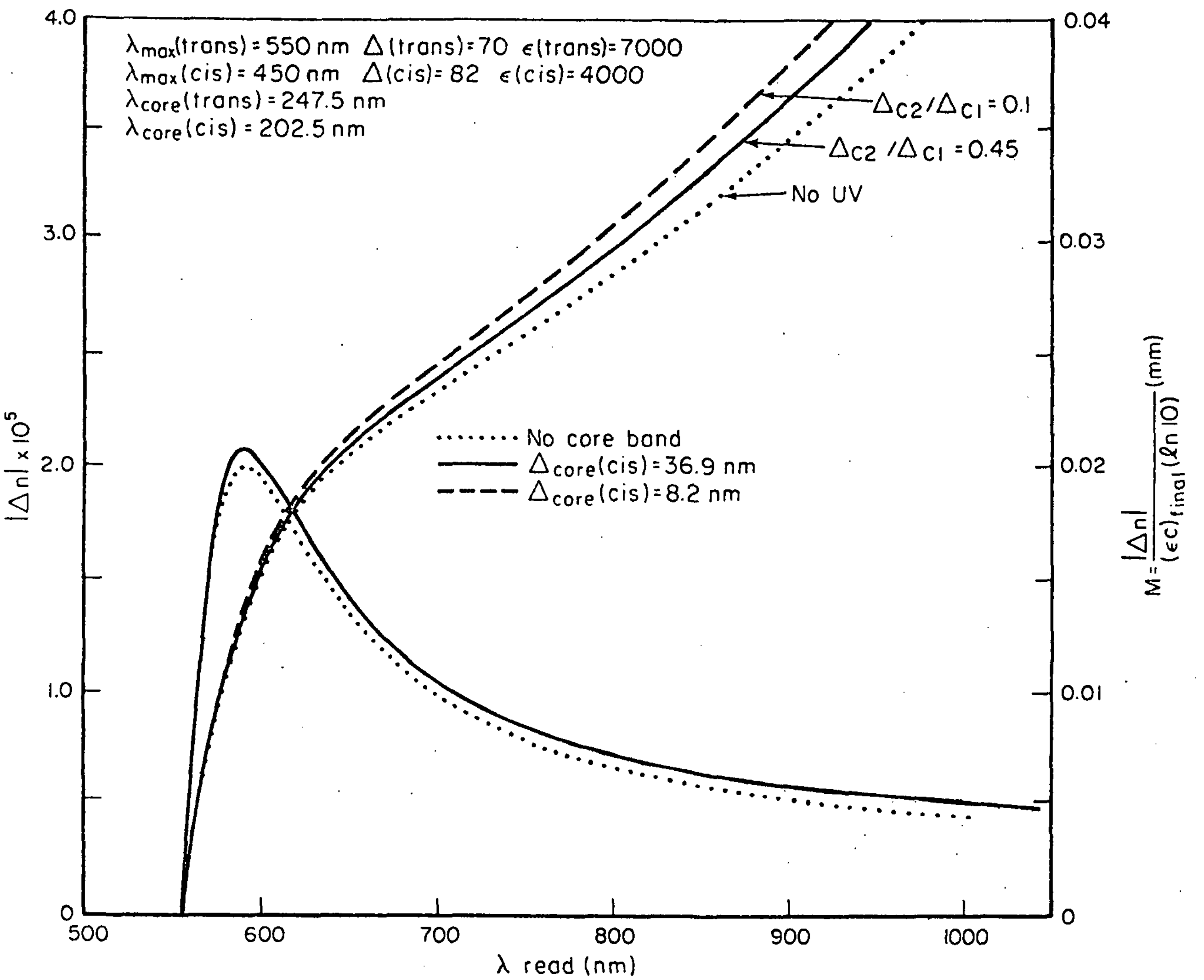


FIGURE 9. THE EFFECTS OF THE SHIFT OF A CORE BAND ON THE CHANGE IN REFRACTIVE INDEX AND FIGURE OF MERIT

Figure 8 reflects the fact that Δn depends only on the difference in the fraction of molecules in the cis and trans states and thus is the same in each case. However, the figure of merit is rather sensitive to the actual fractional values with the greater improvement affected by the last molecules to be converted. This result is easy to understand,as each molecule making the transition from the trans to the cis state reduces the final state absorption and consequently increases the figure of merit.

Finally, in Figure 9, the results of including an additional core band in the vacuum UV are shown; it is seen that inclusion of a band with the same oscillator strength as the main absorption bands (in the visible or near UV) results in only a small change in refractive index or figure of merit. Changes in bands very far from the reading wavelength will produce a small change in refractive index independent of the widths of these bands; for core bands of the same strength as the writing bands, the increase in magnitude of the change of refractive index amounts only to about 4%. For the model in which the band absorption is Lorentzian, there will always be some absorption associated with these core bands and this will be smaller the narrower these bands. However, this absorption is small in any case and is more than offset by the change in refractive index.

Thus, the theoretical analysis offers no real surprises. However, this work has allowed a quantification of intiutive considerations and thereby provides the needed guide to the choice of potential materials for the recording of phase holograms.

EXPERIMENTAL PROCEDURE

Experimentation leading toward the development of a photochromic holographic recording material encompassed both the synthesis (or acquisition) and evaluation of a variety of compounds: stilbenes, thioindigos, indigos and several compounds exhibiting valence isomerization. Solubility, refractive index characteristics and absorption spectra were determined for each compound. Photochemical studies demonstrated the importance of matrix viscosity and concentration in affecting quantum yield of photoisomerization. Holographic gratings were written in those materials with the best combination of properties, and diffraction efficiencies and required writing energies were measured.

Synthesis of Candidate Materials

During the course of this research, the following compounds were prepared for evaluation.

1. trans-4-Methoxy-4'-nitrostilbene. This compound was easily prepared following the method of Pfeiffer(9). Nitrophenylacetic acid was reacted with 4-methoxybenzaldehyde in the presence of piperidine. This was heated with refluxing for one hour and recrystallized several times from hot acetic acid. Excess acid was removed by slurrying a chloroform solution of the stilbene with a weak aqueous sodium carbonate solution for several hours. Evaporation of the chloroform from the organic layer was followed by recrystallization from hot ethanol. Yield was 60%, melting point 130-132 C.

2. cis-4-Methoxy-4'-nitrostilbene. The cis isomer of 4-methoxy-4'-nitrostilbene was prepared by irradiating 500 ml of a 5.0×10^{-3} M solution of the trans isomer in benzene in an Ace Glass photochemical reactor using a 450 watt medium pressure Hanovia mercury lamp in a quartz glass shield ($\lambda > 360$ nm). The irradiated sample was concentrated by vacuum. Isomers were separated by column chromatography on neutral alumina using ether/hexane (1:1) elution. Chilling of the cis-eluate prior to solvent evaporation *in vacuo* gave bright yellow cyrstals which did not require the difficult recrystallization from hot ethanol. This method

gave 20% yield of a product, 95% cis-isomer as verified by high pressure liquid chromatography (HPLC).

3. cis and trans-4-Methoxy-4'-nitro-α-methylstilbene. The original synthetic work with this compound involved a Meerewein-diazonium coupling of p-methoxy-α-methylstyrene and p-nitroaniline. This long procedure gave, at best literature report, only 30% yield. Synthetic studies of this compound for this phase of the program, therefore, concerned alternate methods for obtaining the stilbene in higher yields.

The most promising method was a Wittig reaction described by Ketcham, Jambotkar and Martinelli.(10) Under very dry conditions, nitrophenylmethylenetriphenylphosphorane, a primary precursor, was prepared by reaction of nitrophenylchloromethyltriphenylphosphorane with sodium dimethylsulfonate (DMSO heated with sodium hydride) in benzene. This product was reacted with 4-methoxyacetophenone for 8 hours. Crude product was extracted from a bright orange solid with petroleum ether and recrystallized from hot ethanol. A 55% yield of the desired bright yellow product was verified by infrared spectroscopy. Efforts to scale up the synthesis were shelved when the superior refractive index properties of the more easily prepared 4-methoxy-4'-nitrostilbene became apparent. The cis/trans ratio of the product was not established.

Only chromatography separation on alumina followed by recrystallization from hot ethanol was necessary to isolate a reasonable quantity of the cis-isomer from the mixed isomeric product of the 4-methoxy-4'-nitro-α-methylstilbene synthesis.

4. 4,4'-Dinitrostilbene-2,2'-Disulfonic Acid. This material was obtained as a crude commercial sample from American Cyanamid Corporation and recrystallized from hot aqueous ethanol with the use of decolorizing charcoal. The resulting bright yellow salt was soluble in water to the extent of 73% and had a melting point greater than 360 C.

5. trans-4-Methoxystilbene. This was prepared, primarily for spectral reference, after the method of Orekhoff and Tiffeneau.(11) The starting compound 4-anisylbenzylcarbinol was prepared by Grignard reaction of tolylmagnesium chloride (from α-chlorotoluene and magnesium) and

4-methoxy benzaldehyde. This was then dehydrated using sulfuric acid and the product was recrystallized from hot ethyl acetate. The snow white crystals melted at 134-135 C. Yield 60%.

6. N,N'-dibenzoylindigoid dyes. All of these derivatives were prepared by the method of Posner.(12) The appropriate benzoyl chloride was added to pyridine. Indigo was added with stirring and the mixture was heated to reflux temperature and held several hours. The desired indigo derivative was then purified by hot filtration (to remove unreacted indigo), followed by removal of the solvent *in vacuo* and recrystallization of the residue from ethanol, acetic acid, or acetonitrile, as appropriate.

7. $\Delta^{2,2'}$-Bis-(2H-1,4-benzothiazine). This parent compound was synthesized according to method of B. L. Kaul.(13) Dichloromaleic anhydride was reacted with 2-aminobenzenethiol in acetic acid under reflux conditions for *ca*. 20 hours. The crude, orange product, which was produced in high (53%) yield, was insoluble in all solvents tried. Acylation produced a derivative which was no more soluble than the parent.

8. 3,4,5-Trimethoxy-α-phenylfulgide.

(a) Diethyl isopropylidene succinate. Acetone was reacted with diethylsuccinate under anhydrous conditions in a potassium-t-butoxide and t-butanol solution. Refluxing for 1-1/2 hours, followed by appropriate work-up procedures described by Overberger and Roberts,(14) produced the half-ester as white crystals. The diester was prepared under anhydrous conditions by passing hydrochloric acid gas through an ethanol solution of the half-ester. The mixture was allowed to stand for 24 hours, and the product was then extracted into ether and isolated.

(b) 3,4,5-Trimethoxy-α-phenylfulgide. A second potasium-*t*-butoxide reaction of the diester with an equimolar amount of 3,4,5-trimethoxy benzaldehyde produced another half-ester/half-acid compound. This was hydrolized in a 10% solution of potassium hydroxide in aqueous ethanol and the diacid was precipitated with hydrochloric acid. Continuing with the method of Heller and Megit,(15) the anhydride was formed by boiling the diacid in acetyl chloride for 1 hour. A green oil, from which several products were isolated, separated from the recommended recrystallization solution of benzene/petroleum ether.

9. Research Gifts. The following compounds were generously donated for this research by the scientists noted.

(a) 6,6'-Diethoxythioindigo: from Prof. George M. Wyman (University of North Carolina).

(b) 15,16-Dimethyldihydropyrene: from Prof. Virgil Boekelheide (University of Oregon).

(c) Bis-(anthracene-9,10-dimethylene): from Prof. Guilford Jones, II (Boston University).

(d) Dianthrylcarbinol: from Prof. Guilford Jones, II (Boston University).

(e) Dianthrylethane: from Prof. Guilford Jones, II (Boston University).

(f) Dianthrylmethane: from Prof. Guilford Jones, II (Boston University).

Sample Preparation

While intial photochemical studies of dyes in chloroform or benzene were easily performed in standard quartz cells, different matrix materials required the development of special methods for preparing and confining the samples. Various considerations in this process included ease of introducing the sample, capacity for degassing, prevention of solvent evaporation and sample leakage, and physical compatibility with irradiation apparatus and spectrophotometer. Incorporation of the dyes into solid polymer matrices presented additional challenges in solubility, chemical compatibility, and homogeneous dispersion of the dye.

Liquid Samples

An initial cell modification was the use of a cork stopper fitted with a needle and exit port for continuous flushing of solutions in standard spectrophotometric cells with argon or nitrogen during irradiation. It was anticipated that this would both stir the solution during irradiation with narrow beams of laser light and reduce the probabilities of oxygen quenching and/or side reactions. This approach proved to be ineffective for long irradiations because the evaporating solvent left solid dye which clogged the needle. The method was also unsatisfactory for viscous solutions. In subsequent experiments, the laser beam was expanded to cover the cell surface, and degassing was performed before irradiation.

Viscous gel solutions were prepared by adding solid polyisobutylene (Vistanex MM/L-120 and MM/L-140) to benzene or toluene in a jar and bubbling argon through the mixture for an hour to remove dissolved oxygen. The jar was then tightly sealed and placed on a rolling mill for several days until the polymer had dissolved. Known amounts of stilbene or indigoid dyes were added to the polymer from benzene or toluene solutions.

Disposable, 1.0-cm Pyrex cuvettes were made for the initial irradiation studies. The absorbance of the samples was typically too great, however, for laser studies at that thickness. Therefore, 1-millimeter thick samples were prepared under argon by clamping the polymer solutions, confined by a 1-mm thick Teflon spacer, between two glass microscope slides and sealing the edges with epoxy.

Irradiation studies revealed extreme degradation of certain stilbene derivatives in toluene solution and some similar degradation in benzene. On the assumption that the dyes were reacting photochemically with impurities in the solvent, the benzene for subsequent experiments was purified by photochlorination*(16) and distillation. No appreciable degradation was observed in the purified benzene solutions.

Gels

Readily available, water-soluble gels were the first choice for this phase of study. Considerable time was devoted to purification

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* Ultrapure benzene can be prepared by brief irradiation of commercial benzene saturated with chlorine gas;(12) this converts any olefinic aliphatic, or heterocyclic impurities to high-boiling chlorinated compounds which may be removed by chromatography and distillation.

and photochemical analysis of the water-soluble sodium salt of 4,4'-dinitrostilbene-2,2' -disulfonic acid. Spectral changes were observed upon irradiation of this compound in water, but IR spectroscopy gave evidence of conversion to another compound, perhaps the free acid.

Polysar Butyl XL-20 was the first gel tested. A granular sample of the gel was swelled in benzene, rinsed, dried, and placed in a concentrated solution of stilbene. Excess dye solution was drained off and the cis-isomer was detected following irradiation in this matrix. Furthermore, with enough solvent to maintain transparency of the granular gel, diffusion of the dye was a problem. Diffusion rate was estimated by placing crystals of Rhodamine B, a larger dye molecule than stilbene, in a glass slide cell with the gel. Within 4 hours the dye had become evenly distributed throughout the gel matrix.

The next gels employed were sheets of ethylene/propylene/diene terpolymer and ethylene/propylene copolymer, both with a dicumyl peroxide cure. The latter retained more dye when it was dissolved in a solution containing the dye, but it was tacky and difficult to handle; the terpolymer was therefore favored for subsequent experiments. Care was taken to remove impurities in the gel by extracting it with a graded series of mixtures of methanol and benzene, ranging from pure benzene to pure methanol, in a Soxhlet extractor for a period of several days.

The glass slide cells could not be made to adequately prevent the gel samples from eventually drying, despite the attempted use of a variety of sealants (epoxy, silicon rubber, and various commercial products. These cells were replaced by cylindrical, stainless steel, screw-type cells with quartz windows, as illustrated in Figure 10. Using this type of cell, it was possible to retain the solvent in gel samples almost indefinitely. This provided a convenient solution to the vexing problems of drying and shrinkage of the gels. Reversible, true isomerization gratings were successfully written in both 6,6'-diethoxythioindigo and in N,N'-diacetylindigo in the terpolymer gel, using the improved cells. Testing was then begun with solid polymer matrix materials.

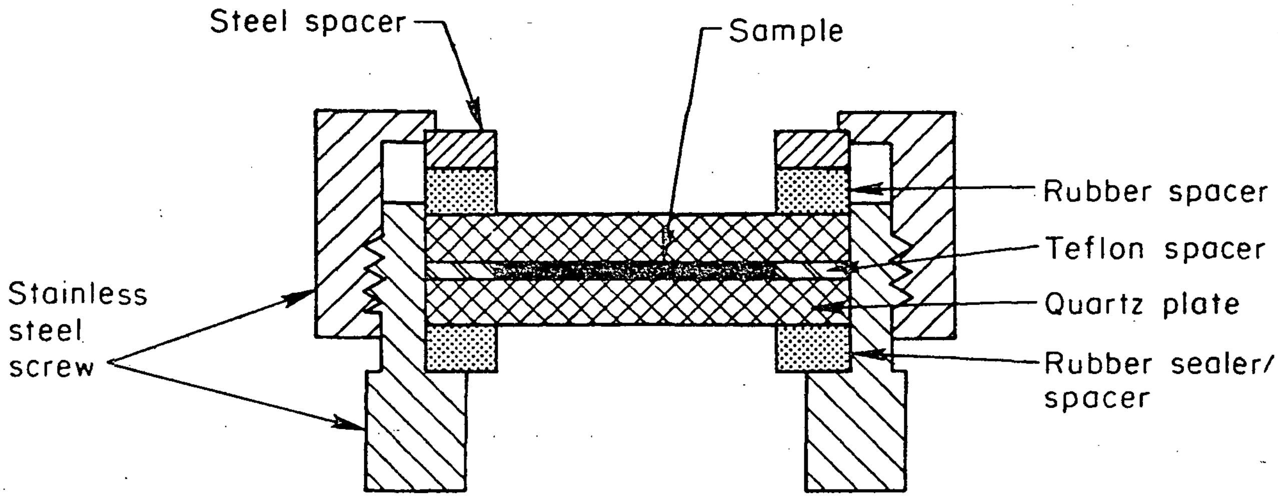


FIGURE 10. SCREW TYPE CELL DESIGNED TO LIMIT EVAPORATION OF SOLVENT FROM GEL MATRICES

Solid Samples

In the early stages of research, when the 4-methoxy-4'-nitrostilbene first was shown to have suitable index change, several solid matrix materials were tested. Methylmethacrylate/styrene/alkyd terpolymer, with melamine formaldehyde resin (83:17 ratio) and a p-toluene sulfonic acid catalyst was suitably transparent, but cis-trans isomerization was shown by thin-layer chromatography to have occurred in the dark. The same polymer, without the catalyst, showed a slower isomerization without light; this was thought to be a reaction with oxygen. Attempts to cure the polymers under argon failed. Irradiation of the stilbene in a series of acrylics (Acryloid B-66, B-44, and A-101) produced a darkening of the samples with no evidence of isomerization.

Another effort during the early phases of this study was an attempt to co-crystallize the stilbene with adamantane, which is known to form a crystal structure with relatively large voids. Some indication of successful co-crystallization was provided by IR spectroscopy, but irradiation yielded no evidence of isomerization.

The successful isomerization of 6,6'-diethoxythioindigo in a gel matrix led to studies of this dye in solid polymers. Epoxies were tried first.(17) Each of the several curing agents (amines, amides, aldehydes, peroxides) for Epon 828 resin reacted chemically with the dye to produce a different, highly colored compound. None of the brightly colored polymers showed evidence of isomerization. The dye was insoluble in polystyrene and polymethyl methacrylate.

Incorporation of N,N'-bis(p-trifluoromethylbenzoyl) indigo, Compound 5, (page 80), into melamine methacrylate (Monsanto 720 melamine and Ashland methacrylate) was accomplished by mixing the dye into the liquid resin mixture, and heat-curing the resulting solution. While photoisomerization did occur in this matrix, the solid was cloudy and was not used further.

Compound 5 was successfully incorporated into both polystyrene and polymethylmethacrylate. Dow 666 polystyrene was dissolved in benzene to give a 20% (W/W) solution. The indigo was then added (0.3%, W/W) and the solvent removed in vacuo. This material could be heated and molded with no adverse effects on the indigo. Reversible photoisomerization was verified in this system, using an Eimac xenon arc lamp in conjunction with a monochrometer.

Commercial (Eastman) polymethylmethacrylate, purified to remove stabilizers, was also used successfully. The indigo was dissolved in purified monomer, mixed with purified polymer and treated with a small amount of dicumylperoxide catalyst. The resulting dye-impregnated polymer was hard and clear, and could be cut and polished into optically clear disks (melting and extrusion molding are also possible with this polymer). Reversible photoisomerization of the dye was verified in the cut, polished disks of polymethyl-methacrylate. These disks were then utilized in writing and erasing of holographic gratings without degradation.

In an effort to improve the low quantum yields observed for these dyes in solids three polystyrene resins with low glass transition temperatures were tested as matrix materials. Samples were prepared by softening the polymer on a glass slide within a Teflon ring ca. 3 mm high and 20 mm in diameter. Crystals of dye were dissolved uniformly in the softened polymer and the matrix was cooled. Irradiation studies with N,N-bis(2-furoyl) indigo showed that reversible isomerization occurred, accompanied by progressive degradation.

A group of compounds exhibiting valence isomerization (15,16-dimethyldihydropyrene, bis-(anthracene-9,10-dimethylene), dianthrylcarbinol, dianthrylethane, and dianthrylmethane) were obtained as research gifts toward the end of the contract period, as previously indicated. The first two compounds were compatible with polystyrene matrices, while the rest were examined in polymethylmethacrylate. These compounds were sensitive to heat, light, and chemical reagents, therefore requiring development of the following procedure.

Monomers for the solid matrix were distilled under partial vacuum through a Vigreux head, dried over CaH_2 and stored under argon in a freezer. Dyes were weighed on a microbalance, transferred to Pyrex ampoules, and a solution of free radical initiator in monomer was added, dissolving the dye.

The contents of the vials were purged with argon and frozen in dry ice; then the vials were sealed with a torch. The methylmethacrylate was polymerized slowly over a period of 10 days at room temperature to prevent void and bubble formation. The styrene was polymerized over a period of 2 weeks. During the last 4 days, the temperature was raised 10 C each day, starting at 25 C and finishing at 65 C. Controls without dye were also prepared. Finally, the glass was broken from the samples to obtain smooth, transparent castings which were cut and polished to form disks of the appropriate thickness for photochemical evaluation.

Chemical Analysis

The analysis of irradiated samples was, in some cases, performed using either a Perkin Elmer Model 521 grating infrared spectrophotometer or a Varian Model 4200 high pressure liquid chromotograph (HPLC). These techniques were used primarily as a supplement to optical measurements for those samples in which degradation was suspected. The HPLC procedure proved to be particularly helpful in the analysis of samples containing 4-methoxy-4'-nitrostilbene, as indicated by Figures 11 and 12.

Optical Measurements

Absorption Spectra

Visible and ultraviolet absorption spectra were recorded using either a Beckman ACTA III spectrophotometer or a Cary Model 14 spectrophotometer. Where pure cis and trans isomers of the candidate materials were available, their spectra provided a basis for calculating the concentrations of the individusl isomers in the samples used for evaluation.

Since pure isomers of the thioindigos and indigos could not be obtained, Wyman's procedure(18) was used to calculate the absorption spectra of the individual isomers. Three photostationary states were prepared for each compound, by irradiating solutions with three different wavelengths

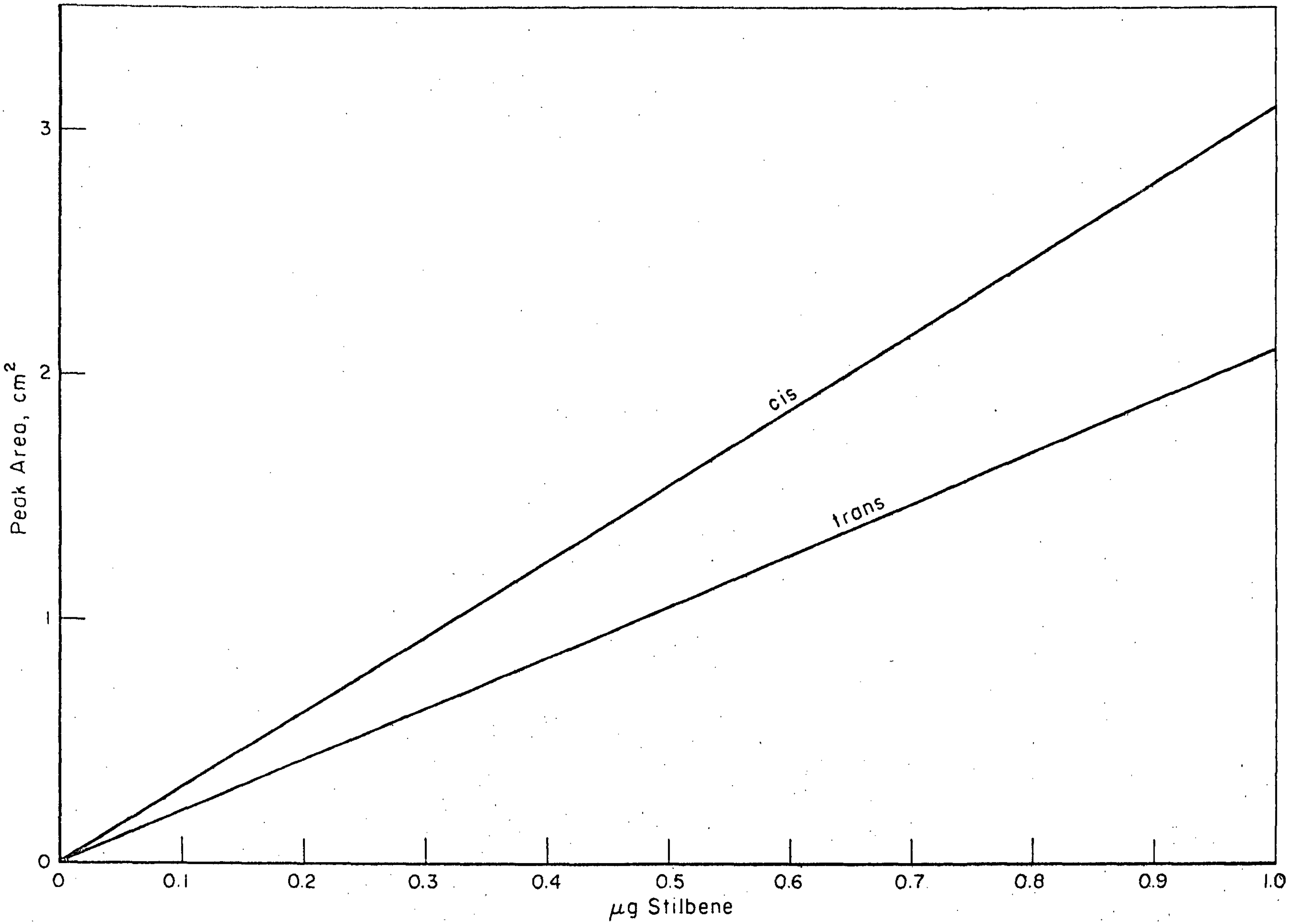
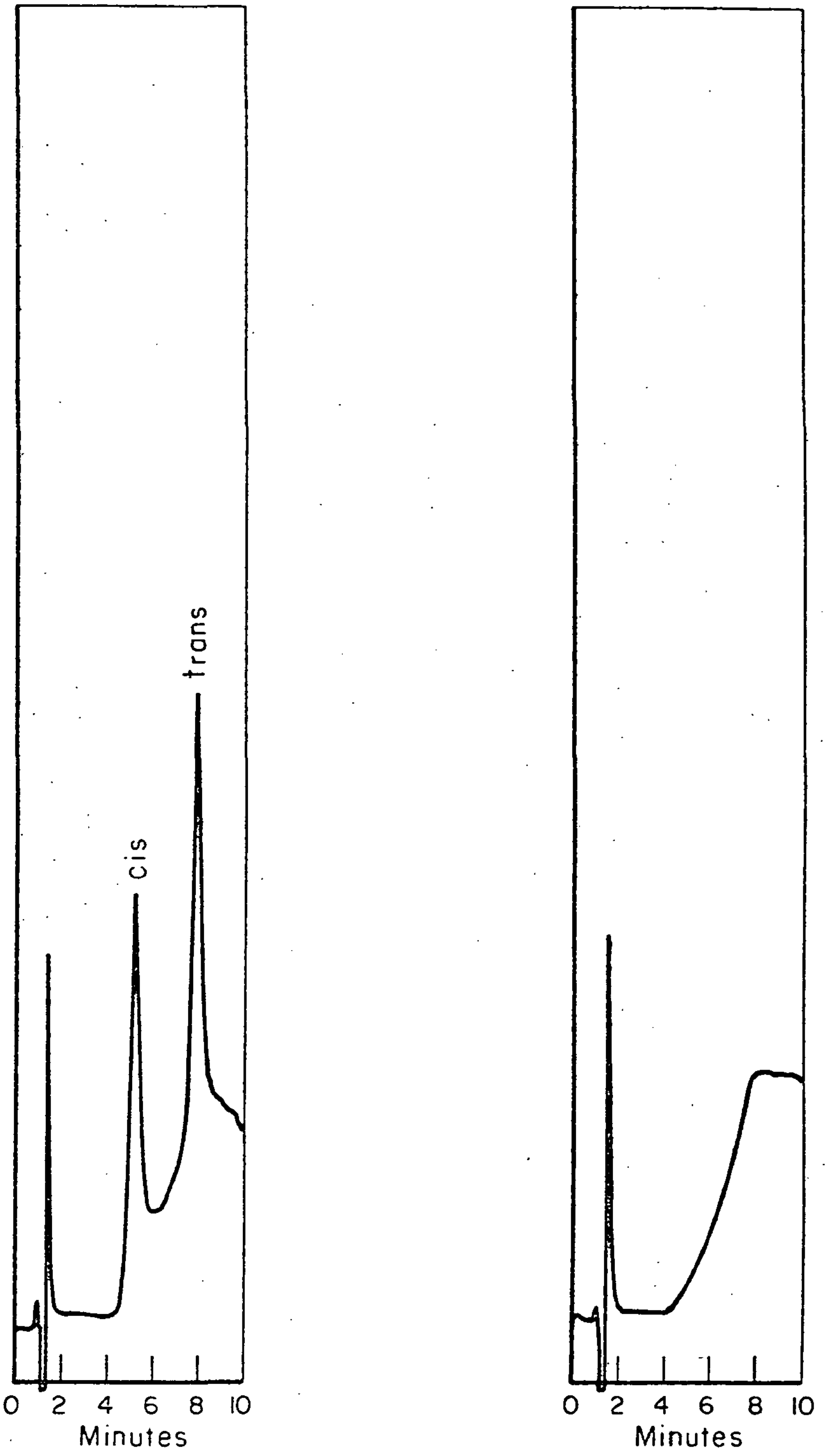


FIGURE 11. HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC) QUANTITATIVE CURVE FOR 4-METHOXY-4'-NITROSTILBENE



a. HPLC spectrum of mixture of _cis_ and _trans_ isomers of 4-nitro-4'-methoxystilbene.

b. Gradient peak of solvent without stilbene.

FIGURE 12. HPLC CHROMATOGRAMS FOR ANALYSIS OF 4-METHOXY-4'-NITROSTILBENE

as shown in Figure 13. Monochromatic light was provided by an Eimac high pressure xenon arc lamp in conjunction with a Bausche & Lombe monochromator. The computer program listed in Figure 14 was written to assist the calculation of spectra from the raw data (Figure 13). A representative set of spectra calculated by this procedure is presented in Figure 15.

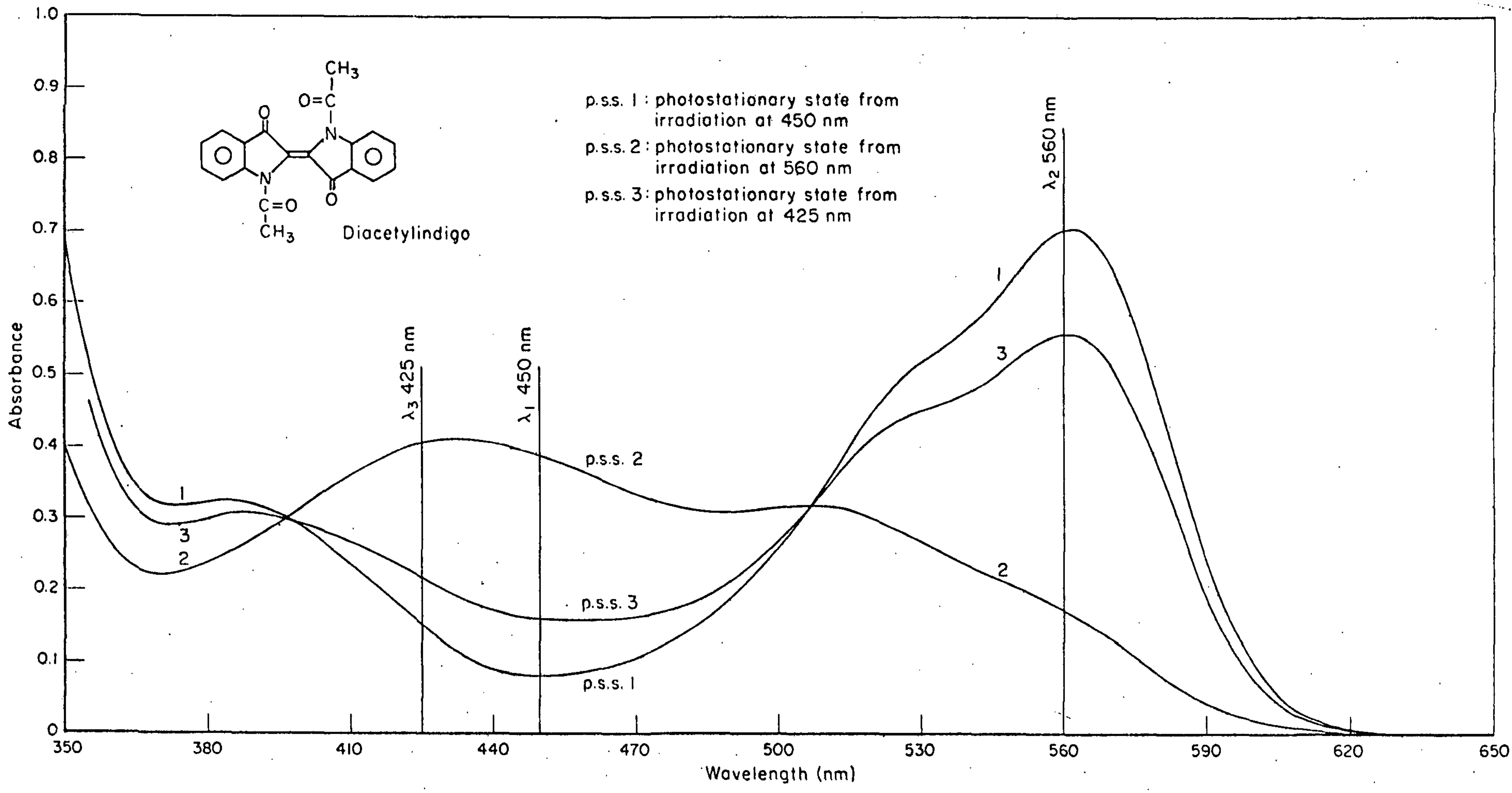


FIGURE 13. ABSORPTION SPECTRA OF THREE PHOTOSTATIONARY STATES OF N, N'-DIACETYLINDIGO USED FOR CALCULATION OF ABSORPTION SPECTRA OF THE PURE ISOMERS

```
00005 DATA .116,.226,.159,440,.718,.437,570,.440,.355,.405,530,1.0E-04
00010 READ K(1),L(1),D(1),W(1),K(2),L(2),W(2),K(3),L(3),D(3),W(3),C
00011 PRINT "IF YOU WANT CALCULATED R, TYPE 0, IF NOT ENTER R."
00012 INPUT R
00013 IF R=0 GO TO 20
00014 PRINT
00015 GO TO 30
00020 R=1.15*K(2)/L(2)
00030 FOR I=1 TO 3
00040 E(I)=(R*L(I)-K(I))/((R-1)*C)
00045 E(I)=INT(E(I)*10^4+.5)/10^4
00050 NEXT I
00055 IF Y>0 GO TO 90
00060 A(2)=(E(1)*L(2)-E(2)*K(1))/(R*E(1)*L(2)-E(2)*K(1))
00065 A(2)=INT(A(2)*10^4+.5)/10^4
00070A(1)=R*A(2)
00075 R1=(K(1)-E(1)*C)/(D(1)-E(1)*C)
00076 A(1)=INT(A(1)*10^4+.5)/10^4
00080 A(3)=R*A(2)/R1
00085 A(3)=INT(A(3)*10^4+.5)/10^4
00090 FOR I=1 TO 3
00100 E(I+3)=((K(I)/C)-((1-A(1))*E(I)))/(A(1))
00105 E(I+3)=INT(E(I+3)*10^4+.5)/10^4
00110 Q(I)=E(I+3)/E(I)*A(I)/(1-A(I))
00112 Q(I)=INT(Q(I)*10^4+.5)/10^4
00120 NEXT I
00121 IF Y>0 GO TO 170
00128 PRINT "QUANTUM YIELD RATIOS FOR R=";R
00130 PRINT Q(1),Q(2),Q(3)
00135 PRINT "NEW R, IF NO ENTER 0";
00140 INPUT X
00141 PRINT
00142 IF X=0 GO TO 170
00145 PRINT
00150 R=X
00160 GO TO 30
00170 PRINT "E VALUES CALCULATED FROM A CONCENTRATION OF" ,C
00175 S=0
00180 FOR I= 1 TO 3
00190 PRINT "EA";I;"=";E(I),"EB";I;"=";E(I+3),"  WAVELENGTH=";W(I)
00196 PRINT "A";I ;"="; A(I)
00197 PRINT
00200 NEXT I
00201 PRINT "TO CALCULATE ADDITIONAL E VALUES, TYPE 1; IF NOT TYPE 0";
00205 PRINT
00210 INPUT Y
00215 IF Y = 0 GO TO 300
00216 S=S+1
00217 IF S>1 GO TO 230
00220 PRINT "ENTER ABSORBANCE DATA FOR TWO PHOTOSTATIONARY STATES"
00222 PRINT"AT EACH WAVELENGTH AS INDICATED AND AWAIT E VALUES"
00230 PRINT
00239 PRINT "ENTER D(1,W), D(2,W), WAVELENGTH"
00240 INPUT K(I),L(I),W(I)
00241 PRINT
00245 E(I)=(R*L(I)-K(I))/((R-1)*C)
00255 E(J)=((K(I)/C)-((1-A(1))*E(I)))/(A(1))
00265 PRINT
00266 PRINT "WAVELENGTH =";W(I);"D(1)=";K(1);"D(2)=";L(I)
00268 PRINT "EA=";E(I);"EB=";E(J)
00269 PRINT
00270 GO TO 201
00300 END
```

FIGURE 14. COMPUTER PROGRAM FOR CALCULATION OF EXTINCTION COEFFICIENTS FROM SPECTRAL DATA

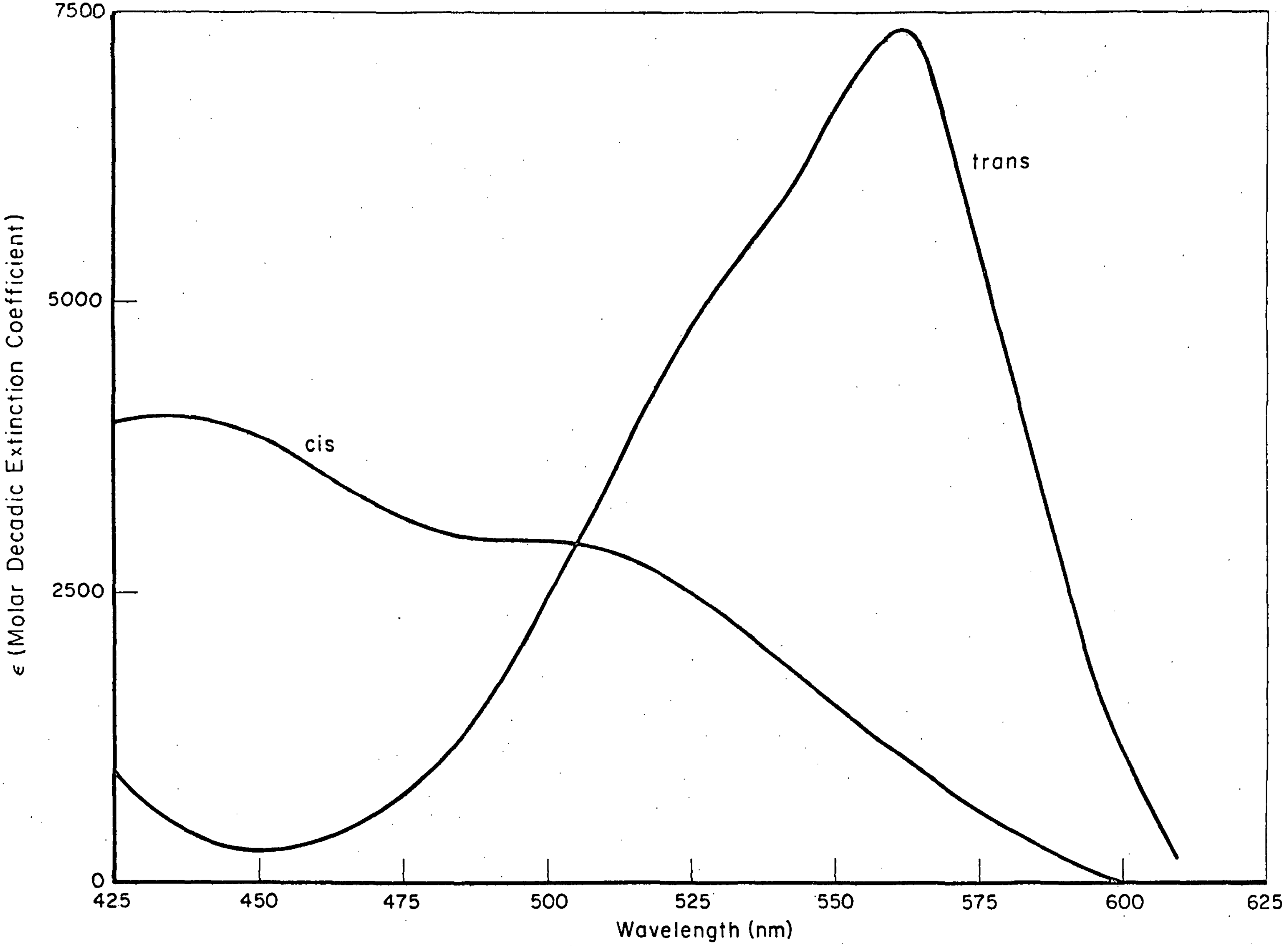


FIGURE 15. CALCULATED ABSORPTION SPECTRA FOR N, N'-DIACETYLINDIGO

Spectroscopic Analysis of Isomeric Composition

Because the refractive index of a solution varies with concentration as well as with the cis to trans isomer ratio, it is essential to know both the total concentration of the solute and the isomer ratio for each photostationary stated used for Δn measurements. These values can be calculated easily from the observed absorption spectra and extinction coefficient data for the pure isomers using the following simultaneous equations, which are derived from Beer's Law:

$$A_1 = A_1^t + A_1^c = \epsilon_1^t \ell C_t + \epsilon_1^c \ell C_c \tag{28}$$

$$A_2 = A_2^t + A_2^c = \epsilon_1^t \ell C_t + \epsilon_2^c \ell C_c \tag{29}$$

where the subscripts 1 and 2 refer to two different wavelengths on the absorption spectrum, and the notations c and t refer to properties of the cis and trans isomers, respectively. A is the absorbance (or optical density), ε is the molar decadic extinction coefficient, ℓ is the optical path length, and C is molar concentration of the solute. Extinction coefficients for the cis and trans isomers of the indigoid dyes were calculated as described previously.

Refractive Index Measurements

The refractive index difference between isomers was the critical property upon which the system for reading holograms was based. Measurements in fluid solution were made with a Brice-Phoenix Differential Refractometer, Model BP-1000 V, either at the sodium D line or at 632.8 nm, using a small helium-neon laser. The refractive index of each isomer was measured against the solvent, usually chloroform, at five different concentrations and against its complimentary isomer at each concentration. Linear plots of refractive index vs. concentration were obtained, as expected; representative results are presented in Figures 16 and 17.

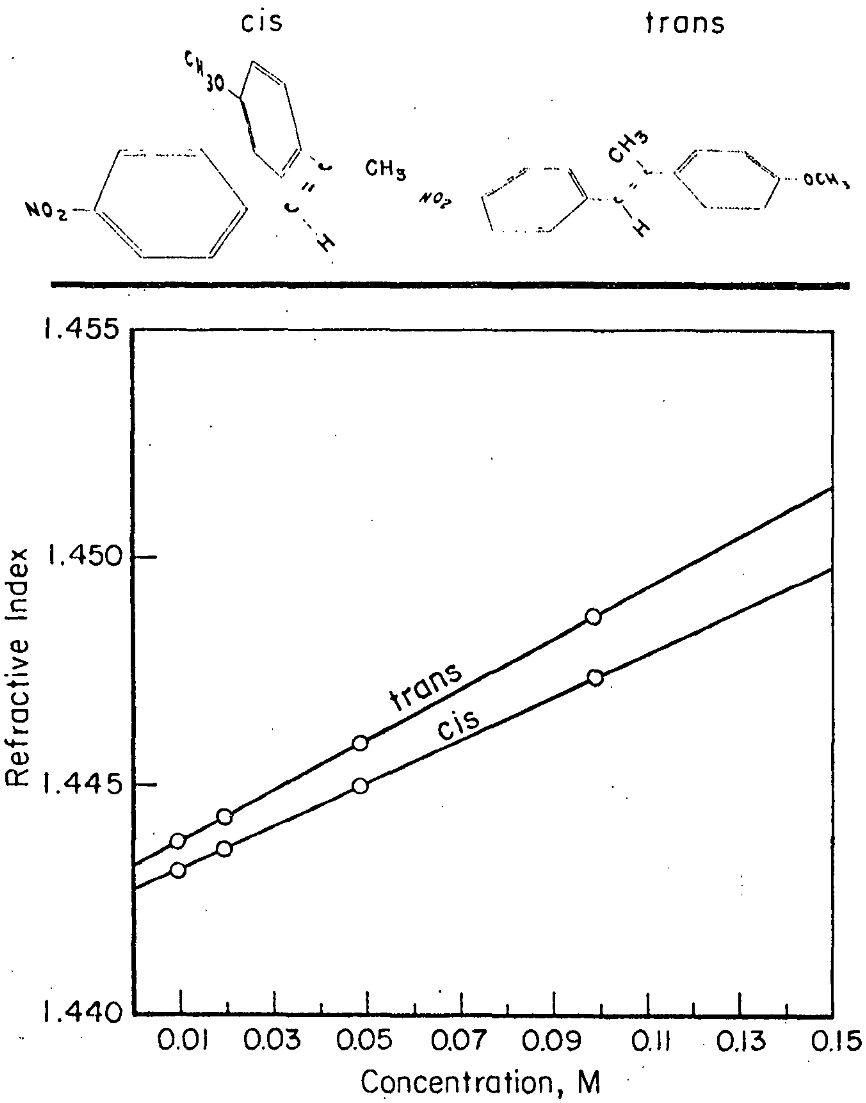


FIGURE 16. REFRACTIVE INDEX AS A FUNCTION OF CONCENTRATION OF cis AND trans ISOMERS OF 4-METHOXY-4'-NITRO-α-METHYLSTILBENE

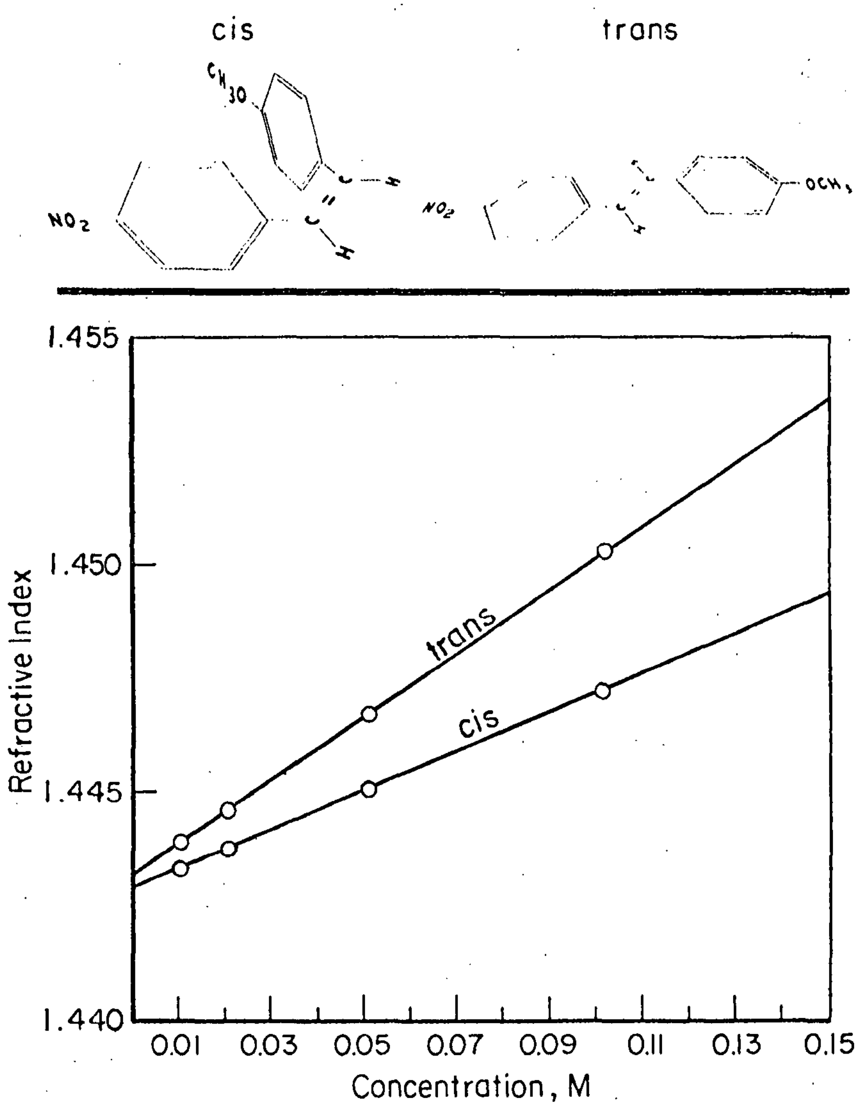


FIGURE 17. REFRACTIVE INDEX AS A FUNCTION OF CONCENTRATION OF cis AND trans ISOMERS OF 4-METHOXY-4'-NITROSTILBENE

Similar analyses of the thioindigos and indigos were not possible because; 1) pure isomers of these compounds could not be isolated, and 2) the poor solubility of the compounds severely limited the accuracy of using the procedure to study photostationary states of known composition. For these materials, the index changes were either calculated from the changes in absorption spectra, as described previously, or were inferred from the diffraction efficiencies observed when holograms were written.

Diffraction Efficiency Measurements

The actual writing of holographic gratings with subsequent measurement of diffraction efficiencies was the ultimate test of the matrix/dye systems. Successful use was made of diffraction efficiency measurements both as a final evaluation of systems, such as the 4-methoxy-4'-nitrostilbene/terpolymer gel matrix, and as a screening method for a series of indigo dyes in polystyrene as the following will describe.

Figure 18 is a diagram of the experimental setup used for a cursory determination of the diffraction efficiencies of holographic gratings formed in sample materials by the interference of two laser beams. The laser beam power of 10 mW is divided about equally between the two interfering beams. Beam diameters are approximately 1.5 mm at the sample surface. Because of very low power levels in the first-order diffracted beam, a narrow-band-pass filter and aperture were placed in front of the detector to exclude extraneous radiation. A UDT (United Detector Technology) silicon detector calibrated for 6328A radiation was employed for power measurements.

Diffraction gratings were formed by interfering the two laser beams at the surface of the 0.5 - 1.0 mm-thick samples. The first-order diffracted beam was monitored by intermittently blocking one of the writing beams until the diffracted power stabilized or decreased with time. The maximum grating efficiency typically occurred within two minutes exposure time.

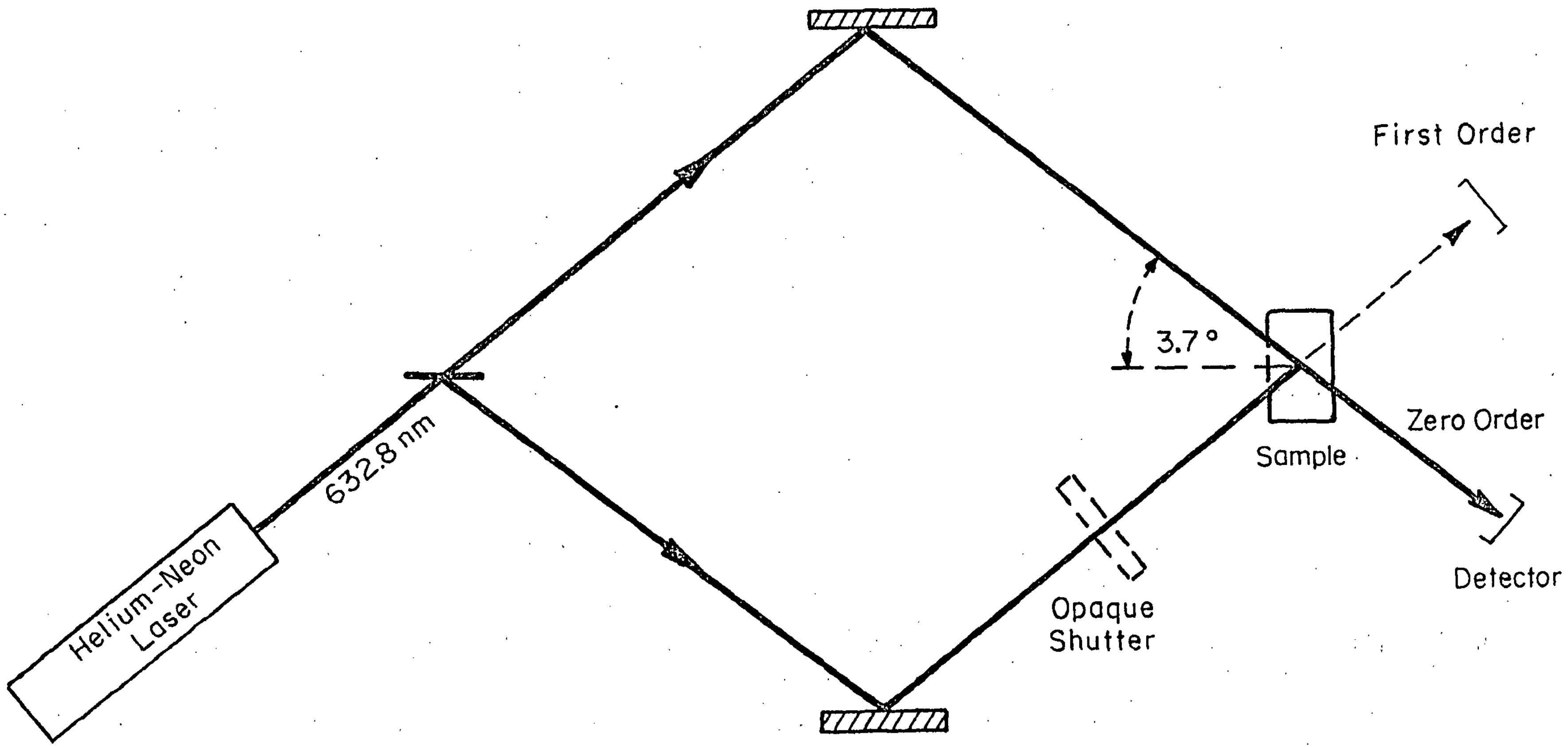


FIGURE 18. DIAGRAM OF APPARATUS USED FOR A CURSORY DETERMINATION OF DIFFRACTION EFFICIENCIES OF HOLOGRAPHIC GRATINGS

Quantum Yield Measurement

In order to evaluate properly the significance of the observed diffraction efficiencies, it was essential to know the extent to which the candidate material had isomerized. The efficiency of photoisomerization is described by the quantum yield (ϕ), which is defined as the number of molecules undergoing the desired photoisomerization per absorbed photon.

Approximate relative quantum yield estimates of liquid solutions were made by comparing the absorption spectra of compounds irradiated for a given length of time with monochromatic light (xenon arc source and monochrometer). Viscosity effects were qualitatively evaluated for the stilbenes by varying the solvent from benzene and chloroform to ethylene glycol, cyclohexanol, glycerine, and finally to viscous benzene/polyisobutylene (Vistanex MM/L-120) solutions.

Thioindigos were isomerized in solution and in gels with no significant change in quantum yield. They were, however, insoluble in, or reactive with, the variety of solid matrix materials tested (PMMA, polystyrene, epoxies, melamine). The quantum yield measurements assumed greater importance once several indigos were shown to isomerize slowly in solid polymer matrices. The conventional method of quantum yield determination proved to be impractical, and a novel method for obtaining this data was derived.

Method

The usual technique for the determination of photochemical quantum yields for the process $A + h\nu \rightarrow B$ involves three steps:

1) chemical or spectroscopic determination of the concentration of A and B in the original sample,
2) irradiation with light of a known intensity monitored in such a way that the total number of photons <u>absorbed</u> is known,
3) redetermination of the concentrations of A and B in the final sample.

The quantum yield, ϕ_{AB} for the photoconversion of A to B is then the number of desired photoconversions per photon absorbed. This method is not only tedious but in the case where light of a given wavelength drives B → A as well as A → B, it is entirely unworkable. This provided the motivation for the development of an entirely different method for measuring the quantum yields ϕ_{tc} and ϕ_{ct} for the cis-trans systems.

The typical cis and trans absorption curves (Figure 15) consist of two broad, partially overlapping bands. Irradiation with monochromatic radiation anywhere within these bands will ultimately drive the system to a photostationary state. Both the rate at which this occurs and the composition of the photostationary state are a function of the irradiation wavelength. The rate equations for this process are:

$$\frac{dN_t}{d\tau} = N_c \; I \; \sigma_c \; \phi_{ct} - N_t \; I \; \sigma_t \phi_{tc} \tag{30a}$$

and

$$N = N_c + N_t \tag{30b}$$

Here N_c (z,τ) and $N_t(z,\tau)$ are the instantaneous, local cis and trans molecular densities in cm^{-3}, I (z,τ) the incident light intensity in photons/cm^2-sec, $\sigma_c(\lambda)$ and $\sigma_t(\lambda)$ the absorption cross sections in cm^2 and ϕ_{ct} and ϕ_{tc} are the quantum yields which, for the materials in question, are independent of wavelength$^{(19)}$. The coordinate z is measured positively into the medium with z = 0 at the front surface. If an infinitely thin sample were under consideration so that all z dependence could be ignored, and the time dependence of $I(z,\tau)$ also could reasonably be ignored, then equations 30 could be combined and solved with result

$$N_t\,(\tau) = \frac{N\sigma_c\,\phi_{ct}}{\beta}[1 - A\;e^{-\beta I\tau}] \quad , \tag{31}$$

where

$$\beta = \sigma_c\,\phi_{ct} + \sigma_t\,\phi_{tc} \quad , \tag{32}$$

and

$$A = 1 - \frac{\beta}{\sigma_c \, d_{ct}} \; \frac{N_t(0)}{N} \tag{33}$$

is the constant of integration.

We can calculate the instantaneous transmission T(t) of a sample of (negligable) thickness d and of arbitrary initial cis-trans ratio as it is driven by light of wavelength λ and intensity I_o to its photostationary state.

$$T(\tau) = I_o - A(\tau) \tag{34}$$

where the instantaneous absorption is given by

$$\begin{aligned} A(\tau) &= [N_T(\tau)\, \sigma_T + N_c(\tau)\sigma]\, I_o\, d \\ &= [N_T(\tau)\, (\sigma_T - \sigma_c) + N\sigma_c]\, I_o\, d \end{aligned} \tag{35}$$

combining Eqs. (34), (35) and (31)

$$T(\tau) = 1 - N\sigma_c d - Nd\, \frac{\sigma_c \phi_{c\tau}}{\beta}\, (\sigma_T - \sigma_c)\, [1 - Ae^{-\beta I_o \tau}] \tag{36}$$

The transmission is therefore characterized by an exponential function with ϕ_{ct} and ϕ_{tc}, the two quantities of interest, in both the exponent and in the coefficients. The following section will discuss the extraction of the quantum yields from the experimental data for this idealized case.

In performing the suggested experiment, that is, monitoring the transmitted light during the trans to cis conversion, the observed variation of $T(\tau)$ with time has the simple exponential form which can be described by the empirical equation

$$T(\tau) = T_s - (T_s - T_i)e^{-Q\tau} \tag{37}$$

It is possible, with the use of Eq. (31), to demonstrate the equivalence of the coefficients in Eqs. (36) and (37). However, it is of more interest to consider the exponential term. We identify Q with βI_o. For any wavelength, Q can be determined from a plot of $\ln[T_s - T(\tau)]$ vs τ, the slope of this plot being $-Q$. If this is done for two wavelengths we have,

$$Q_1 = \beta_1 I_1 = I_1[\sigma_{T_1} \phi_{tc} + \sigma_{c_1} \phi_{ct}] \qquad (38)$$

$$Q_2 = \beta_2 I_2 = I_2[\sigma_{T_2} \phi_{tc} + \sigma_{c_1} \phi_{ct}] \qquad (39)$$

where the numerical subscript indicates wavelength. From (38) and (39)

$$\phi_{tc} = (\frac{Q1}{I_1} - \frac{\sigma_{c1}}{\sigma_{c2}} \frac{Q2}{I_2})/(\sigma_{T_1} - \frac{\sigma_{c1}}{\sigma_{c2}} \sigma_{T_2}) \qquad \text{and,}$$

$$\phi_{ct} = (\frac{Q2}{I_2} - \frac{\sigma_{T2}}{\sigma_{T1}} \frac{Q1}{I_1})/(\sigma_{c2} - \frac{\sigma_{T2}}{\sigma_{T1}} \sigma_{c1})$$

The required values of σ can be obtained from spectrophotometric data on each of the pure samples or, from <u>cis-trans</u> mixtures using the method of Wyman(14).

In the above discussion it was assumed for the sake of simplicity that the sample is so thin that concentration and intensity variations through its depth could be ignored. In fact, in order to take meaningful data, it is necessary to use samples which are thick enough to introduce a significant z dependence to I. The errors in the above treatment which result from ignoring this dependence can be limited to about a factor of two by using samples with maximum optical densities of about 0.2. The relative values of ϕ determined in this way are still therefore quite useful in screening compounds and especially in evaluating host and concentration effects. For more precise work one can use the more complete treatment recently developed by Tomlinson(20). In order to use this theory, it is necessary to measure accurately the initial absorption, the absorption in the quantum stationary state and at least one intermediate point (although measurements at a number of intermediate values can, of course, give more satisfactory results). The ratio of the initial absorption to that in the quantum stationary state gives a parameter in Tomlinson's theory; solution of a transcendental equation for intermediate values of time gives values for the quantity

$$I_0 (\sigma_c \phi_{ct} + \sigma_t \phi_{tc}) \quad , \qquad (40)$$

where I_0 is the incident intensity, a known quantity. It is straightforward to determine the populations N_c and N_t in the quantum stationary condition by setting equation 30a equal to zero;when this is done, the absorption coefficient for this distribution is

$$\alpha_s = \left[\frac{\sigma_c \sigma_t (\phi_{ct} + \phi_{tc})}{\sigma_c \phi_{ct} + \sigma_t \phi_{tc}} \right] N \tag{41}$$

Thus, since the total concentration of diluent molecules is also a known quantity,these measurements give information about the quantitites

$$u = \left[\frac{\sigma_c \sigma_t (\phi_c + \phi_t)}{\sigma_c \phi_{ct} + \sigma_t \phi_{tc}} \right]$$

and

$$v = \sigma_c \phi_{tc} + \sigma_t \phi_{ct}$$

Thus, given independent measurements of the cross sections σ_c and σ_t, it is finally possible to calculate the quantum yields

$$\phi_{ct} = \frac{(u - \sigma_c)\ v}{\sigma_c\ (\sigma_t - \sigma_c)} \quad ,$$

and

$$\phi_{tc} = \frac{v - \sigma_c d_{ct}}{\sigma_t}$$

Apparatus. Figure 19 is a diagram of the experimental setup for determining the value of the response parameter Q, of the trans → cis conversion in a material. The dye laser used was a Coherent Radiation Model 490, pumped by a Coherent Radiation Model 52A argon-ion laser. With a nominal pumping power of 2 W, the maximum dye laser beam power was about 0.2 W; the power was, of course, dependent upon the dye used and the wavelength selected. The power of the dye laser beam was monitored as shown during each experiment to permit corrections to the data should the power vary during a prolonged exposure, viz. tens of minutes.

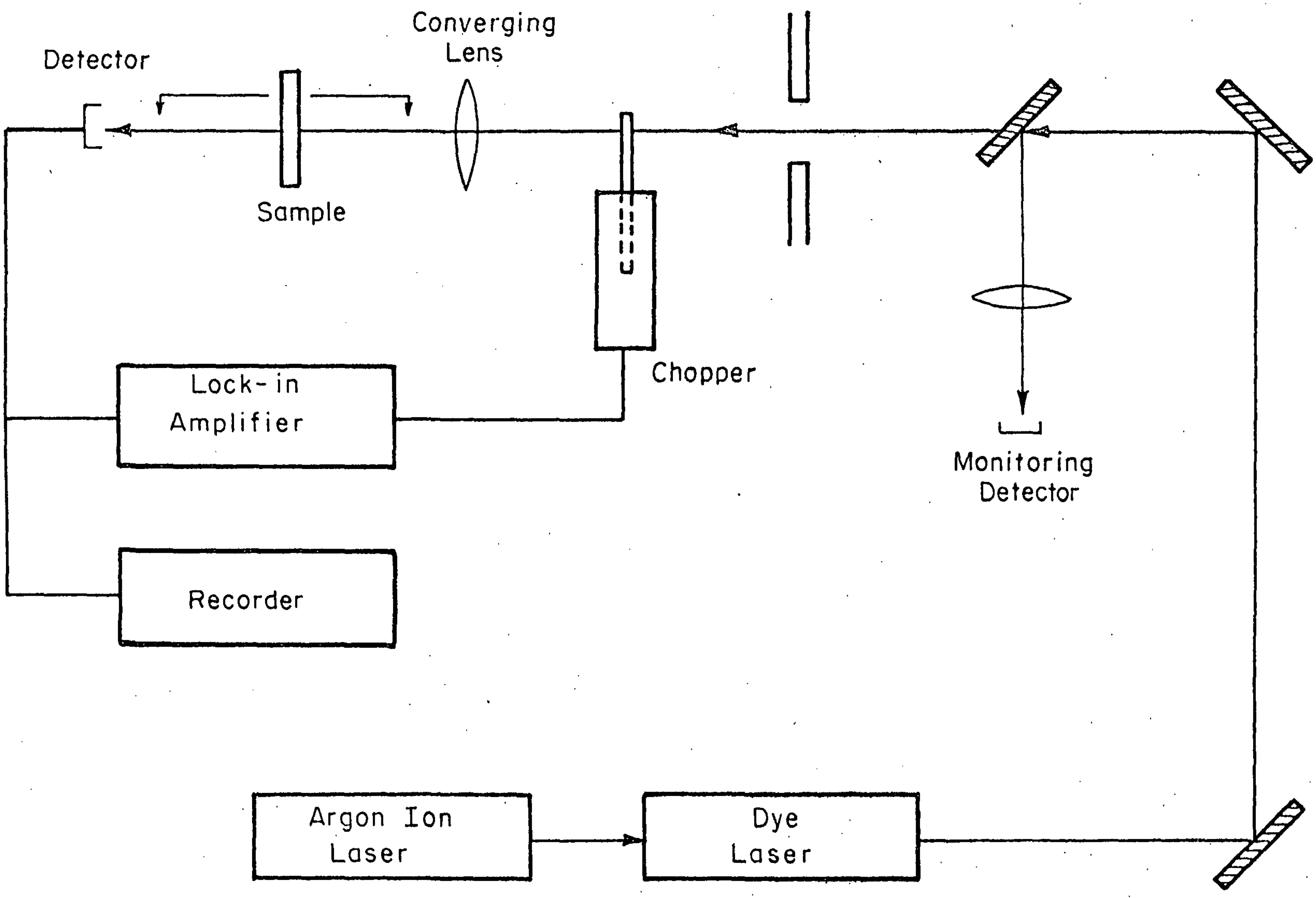


FIGURE 19. EXPERIMENTAL SETUP FOR DETERMINING THE RESPONSE TIME FOR <u>cis-trans</u> MATERIALS

Radiant power measurement was performed using a Spectra Physics Model 210 power meter. For measurements where the signal-to-noise ratio was less than 50, a Princeton Applied Research Model lock-in amplifier was used with radiation chopped at 13 or 28 Hz. For higher ratios, the detector was connected directly to the recorder and the radiation was not chopped. The recorder was a Hewlett-Packard Model pen-type recorder with Model 17108 AM Time Base.

Quantum Yield Studies

The value of Q was measured using the following procedure:

1) The dye laser was tuned to a wavelength within the absorption band of the trans isomer.
2) The power incident on the samples was determined by measuring the unobstructed-beam power.
3) The surface reflection and bulk absorption losses of a reference sample of the matrix alone were determined by measuring the radiant power transmitted by a reference sample consisting of pure matrix material. (A repeat measurement with a reference sample of substantially greater thickness will provide data for separating the two types of loss). Equivalent losses were assumed for the doped samples of interest here.
4) With the beam blocked, the sample was placed at the desired location. The beam was unblocked and the transmitted power was recorded as a function of time until saturation occurred, i.e., the photostationary state was attained.
5) The value of Q for the wavelength used in the irradiation is determined from a semi-log plot of the data. Repeating the measurement with a different wavelength yields a second value of Q. The trans → cis and cis → trans quantum yields can now be determined using the method discussed above.

This system was used not only to investigate the effect of viscosity on quantum yield, but also the effect of concentration. In one experiment, four samples of the same indigoid dye were prepared to have the same optical density; two solid samples of different concentration and thickness and two liquid samples with similar differences in concentration and thickness. The dilute samples had greater quantum yields than the concentrated samples and quantum yield data for both liquid samples were greater than data for either solid sample.

SELECTION AND EVALUATION OF MATERIALS

Materials Selection

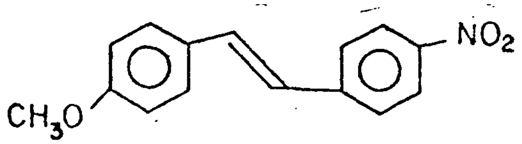
The theoretical and experimental phases of this program were conducted in parallel, for the most part, so the criteria governing the selection of candidate materials evolved continuously as the program progressed. The overriding concern throughout was to identify materials which would combine high sensitivity with the key property of reversibility. The selection of the stilbenes for initial evaluation was based largely on the fact that these compounds had been studied extensively,(3,4) so their photochemistry was well characterized. Several stilbene derivatives were acquired for this program, and were evaluated in a variety of polymeric matrices. These experimental studies showed that the spectroscopic and photochemical properties of the stilbenes were not optimally suited to holographic recording. The focus of the program then shifted to indigoid dyes; this class of compounds had also been studied in some detail,(5,6) and had spectroscopic properties which preliminary calculations indicated to be more favorable for information storage than those of the stilbenes. Several derivatives of indigo and thioindigo were acquired and evaluated both in fluid solution and in polymeric matrices. These materials show considerable potential for reversible holographic recording, but presently suffer from low quantum yields for photoisomerization in the polymeric matrices. The theoretical calculations, meanwhile, have led to the conclusion that materials even superior to the indigoid dyes can be developed. In fact, several classes of compounds which exhibit valence isomerization, rather than cis-trans isomerization, have properties close to those required by the BORAM system. The photoisomerization of these compounds is characterized by absorption shifts from the red (ca. 600-650 nm) to the near-ultraviolet (260-360 nm), with correspondingly large changes in refractive index. Examples are the fulgides(15,21,22) and derivatives of the 15,16-dialkyldihydropyrenes.(23-25) While little experimental evaluation of these materials has been conducted in the course of this program, their properties are sufficiently promising that a summary of their behavior has been included below. Finally, a brief evaluation of lithium niobate was carried out for comparison to the organic materials. The results of these studies are discussed below.

Materials Evaluation

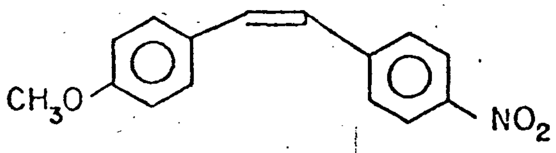
Stilbene Derivatives

Before any experimental work was carried out, careful consideration was given to anticipated refractive index differences between *cis* and *trans* isomers of substituted stilbenes. This resulted in an initial selection of several candidate stilbene derivatives for the holographic system. In a very qualitative sense, the refractive index is dependent upon the compound's electron polarizability, which in turn is a function of the π-bond conjugation. Therefore, a difference in refractive index between *cis* and *trans* isomers is dependent upon a change in polarizability. The conjugation in the π-electron system is much less effective in the non-planar *cis*-isomer than in the *trans*-isomer, which is usually close to a planar configuration. This results in a predictably lower polarizability; or refractive index differences between the *cis* and *trans* isomers depend upon increasing the polarizabilities of the individual isomers, an effect easily accomplished by adding polar groups to the molecule. In such cases, the refractive index of the *trans*-isomer generally increases to a greater extent than that of the *cis*-isomer, thus increasing the magnitude of the refractive index difference. The combination of nitro (NO_2) and methoxy (CH_3O) groups at opposite ends of the molecule is particularly effective in this context. These effects, of course, parallel the changes in absorption spectra induced by the substituents.

Such considerations led to a shift of emphasis away from the α-methylstilbenes because the α-methyl group causes a decrease in planarity of the *trans*-compounds and thus a corresponding decrease in their polarizability. This would be expected to decrease the resulting refractive index differences, and this was confirmed experimentally. Thus, 4-methoxy-y'-nitrostilbene (8) was ultimately selected as the most promising stilbene derivative for evaluation.



trans-8



cis-8

Refractive Index Measurements. Refractive index measurements were conducted as described in the Experimental Procedures section. From the data obtained by measuring solutions of each isomer against chloroform (see Figures 16 and 17), values for the difference in index between the solutions of the cis and trans isomers (Δn) could readily be calculated. A typical plot of Δn vs. concentration is presented in Figure 20. Such linear relationships were extrapolated to estimate the potential Δn for a 50% (5.85 M) solution for the 4-methoxy-4'-nitrostilbene in a matrix. Assuming that 1) such extrapolation is valid, 2) the quantum yield (events/photon absorbed) for trans to cis conversion is 0.2, and 3) the system can be fabricated so that 1/3 of the writing light is absorbed in producing a hologram of a given thickness, the series of calculations outlined below predicted a Δn_{max} of 0.14 and that 2.6×10^{-3} J/mm^2 of blue light would be required to write a 1% efficient hologram. In fact, however, it proved impossible to experimentally come closer than about two orders of magnitude to the above values of concentration and quantum yield. The calculation described below thus represents a "best case" estimation of required writing energy for this compound.

The index of refraction change required to produce a hologram with a 1% diffractive efficiency is determined from the expression

$$\eta = T \sin^2 \left(\frac{\pi \Delta n t_o}{2 \lambda \cos \theta}\right)$$

where

T is the transmission (2/3),

η is the diffraction efficiency, taken as 1%,

t_o is the hologram thickness, taken as 1000 μ (1 mm)

λ is the wavelength of the read beam (500 nm), and

θ is half the angle between the write and read beam (30°).

The required index change is

$$\Delta n = \frac{2\lambda \cos \theta}{\pi t_o} \sin^{-1} (\eta T^{-1})^{1/2}$$

$$= 3.38 \times 10^{-5}$$

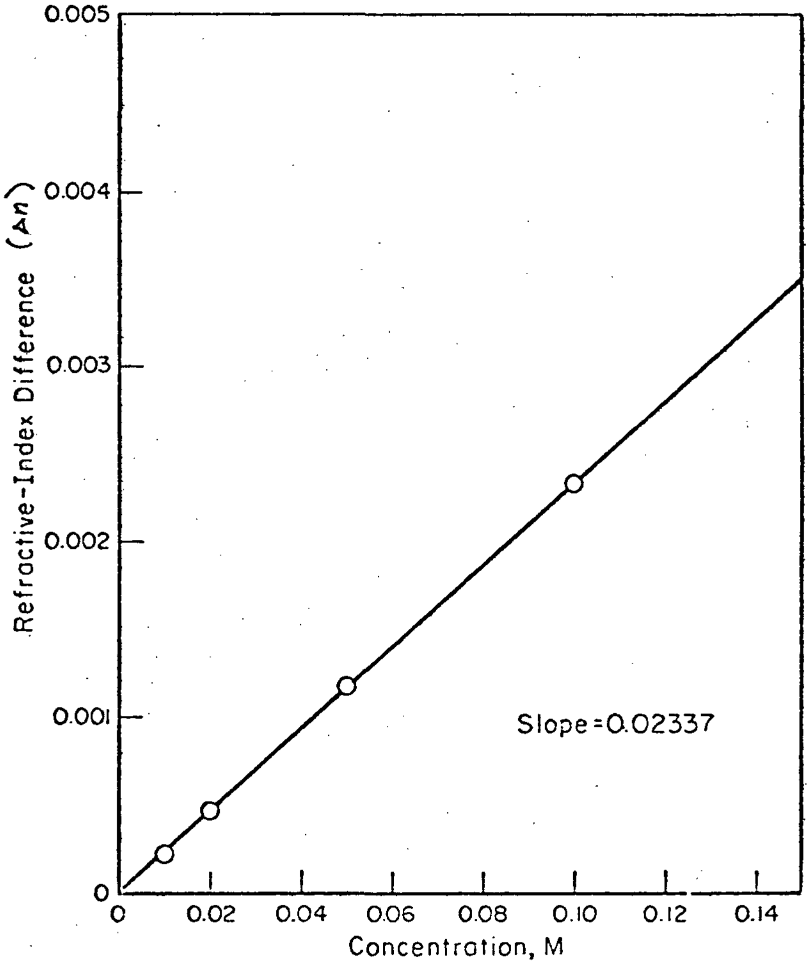


FIGURE 20. REFRACTIVE-INDEX DIFFERENCE AS A FUNCTION OF MOLAR CONCENTRATION OF *cis* AND *trans*-4-METHOXY-4'-NITROSTILBENE IN CHLOROFORM

From Figure 20,it can be shown that to effect this index change in 4-methoxy-4'-nitrostilbene requires that 1.45×10^{-9} moles/mm^3 of the material be switched. The number of molecules which have to undergo the cis to trans-conversion to achieve the required index change is

$$N_m = 6.02 \times 10^{23} \text{ molecules/mole} \times 1.45 \times 10^{-9} \text{ moles/mm}^3 \quad ,$$

or

$$N_m = 8.72 \times 10^{14} \text{ molecules/mm}^3 \quad ,$$

for a 1 mm^3 hologram recording volume. Assuming a quantum yield of 0.2, allowing for absorption of only 1/3 of the light, and noting that molecules in only one-half of the volume are isomerized in forming a typical hologram, it can be seen that a minimal writing energy density (for both beams) of

$$\begin{aligned} E_{write} &\approx 5 \times 3 \times 1/2 \times N_m \text{ photons} \times (3.97 \times 10^{-19} \text{ J/photon}) \\ &\approx 2.6 \times 10^{-3} \text{ J/mm}^2 \end{aligned}$$

must be incident on the one-millimeter-square front face.

Evaluation of Holographic Recording Capability. The research performed during the early phases of this program demonstrated that 4-methoxy-4'-nitrostilbene (8) could be isomerized from trans to cis both in solution and in a benzene/polymer gel system by irradiation with an appropriately filtered xenon arc lamp. The first attempts to write holograms, however, were unsuccessful. These experiments utilized compound 8 in a viscous benzene solution of low molecular weight polyisobutylene, contained between glass slides by a 1 mm thick Teflon spacer. It seems most likely that the failure to write a hologram under these conditions resulted from there being insufficient laser power to isomerize the stilbene at the wavelength used (350 nm). For this reason a more powerful laser (argon ion) was utilized for the bulk of these studies. The laser line at 488 nm was used.

The absorption maximum of trans-8 (the trans form of compound-8) is near 400 nm, but the absorption tails out to nearly 500 nm so there is a small, but finite, extinction coefficient at the 488 nm argon ion laser wavelength. Increasing the stilbene concentration did result in measurable trans to cis isomerization upon irradiation at 488 nm. A stilbene solution of such high concentration (0.10 M) however, had excessive absorbance at the laser wavelengths suitable for erasure; no light was transmitted. Thus, while the cis to trans erasure isomerization may have taken place at the cell's surface, not enough light was transmitted to convert molecules deeper within the sample. This difficulty serves to emphasize the importance of maximizing the refractive index difference (Δn/mole) between the two isomers; the use of high concentrations to compensate for a small Δn/mole (to permit multiple hologram recording) can lead to unfavorable absorbance properties.

During this phase of the research, the threaded sample cell discussed under Experimental Procedures (Figure 10) was designed in an effort to eliminate shrinkage of the gel matrix materials due to slow evaporation of benzene. This system greatly limited the problem of evaporation as well as eliminating the possibility of contamination of the sample by the benzene-soluble epoxies and sealants used on the glass slide/Teflon spacer cell.

Three different polymeric gels, swelled with benzene, were then evaluated as matrix materials:

- Butyl rubber (light sulfur cure) - this gel proved to be soluble in benzene, and was therefore unsatisfactory.
- Ethylene-propylene copolymer (dicumylperoxide cure) - this material was readily swelled in benzene and formed optically clear gels.
- Ethylene-propylene-diene terpolymer (dicumylperoxide cure) - this material also was readily swelled in benzene and formed optically clear gels. As this polymer was the more easily handled, it was used for most of the subsequent studies.

The gels were purified prior to use as described in Experimental Procedures. Disks of the purified gels, swelled in benzene, were placed in concentrated benzene solutions of trans-8 for 24 hours to allow diffusion of the stilbene into the matrix. Irradiation of these samples with a filtered Eimac xenon arc lamp (cutoff below 315 nm), gave no evidence of degradation, as monitored by ultraviolet spectroscopy.

Attempts to obtain high stilbene concentrations (ca. 0.1 M) in the new gels, for continued experiments with 488 nm irradiation, were unsuccessful. There appeared to be a limit to the amount of stilbene which would diffuse into the individual gel disks. When disks of the gels were soaked in aliquots of a benzene solution of known stilbene concentration and analyzed spectroscopically,after equal immersion times it was found that the stilbene concentration varied from sample to sample, even among disks of the same gel. However, stilbene concentrations of ca. 0.03 M could be reproducibly obtained, as determined from the absorption spectra of several samples.

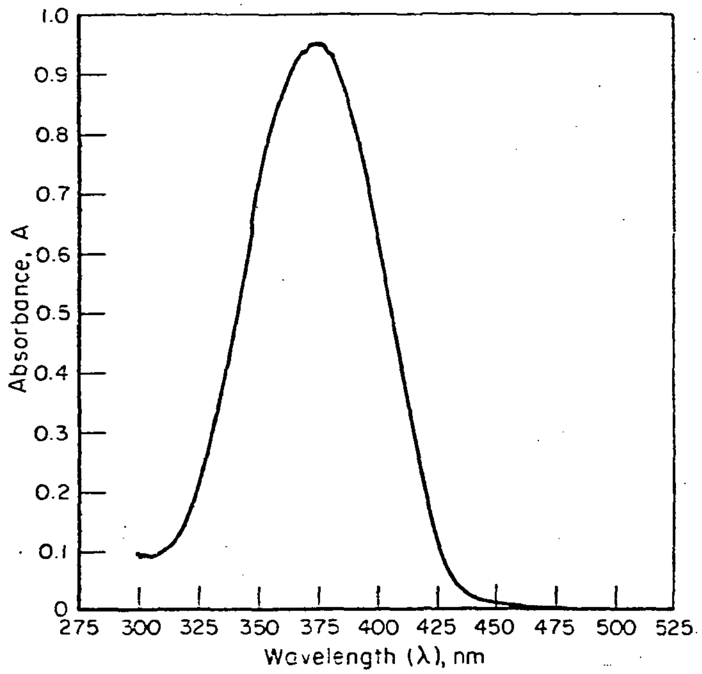
These samples were used to write holographic gratings, using the 488 nm line from the Coherent Radiation argon-ion laser. The presence of the diffracted beam could be observed after approximately three minutes' exposure time. The power of each beam was 3 mw and the beam diameter was 2-3 mm. The approximate half-width of the acceptance angle was 4 minutes, close to the expected value.

The holographic recording capabilities of compound 8, and all subsequent compounds, were evaluated by recording plane wave diffraction gratings in a test sample. A conventional holographic setup, consisting of a laser beam split into two components which then intersected at the site of the recording medium, was used to produce the spatial pattern to be recorded. In all cases the polarization of the writing beam was perpendicular to the plane of incidence.

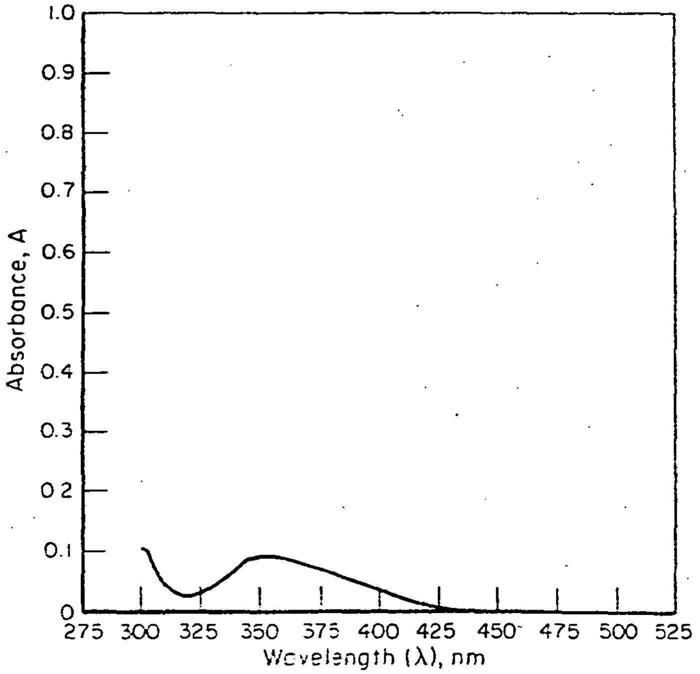
The process of writing the diffraction grating was recorded, in real time, by introducing a second beam, of a wavelength different from that of the writing beam, and monitoring the intensity of its diffracted portion as a function of writing time and energy. Relatively high diffraction efficiencies could be obtained, particularly with the stilbene/terpolymer gel system at a writing wavelength of 457.9 nm. However, it was noticed that none of the holograms written with this system could be erased, and that a brownish spot inevitably appeared at the point of irradiation with the laser beams. These observations strongly suggested that degradation of the system occurred under the conditions of irradiation with the lasers, and it is not known whether the holograms observed with this system resulted from the presence of the desired cis isomer or from the degradation products responsible for the brown spot. However, it is clear from the high diffraction efficiency, that a phase, rather than an absorption, hologram was written.

Degradation. The failure of the samples to undergo erasure could be due, in part, to the strong absorbance of the samples at the wavelengths suitable for erasure, as was mentioned above. The inevitable presence of a brown spot at the point of laser irradiation made it seem quite likely that compound 8 had undergone a photo-induced degradation reaction of some type. The degradation of the stilbene was strikingly confirmed by the disappearance of the absorbance spectrum of the stilbene as the irradiation proceeded (Figure 21). This was thought at first to result from the presence of impurities in the system. However, neither the use of a less unsaturated (and therefore less reactive) gel, high molecular weight ethylene-propylene copolymer (purified by repeated solvent extraction as before), nor the use of photochlorinated benzene, served to reduce the degradation of the stilbene. High pressure liquid chromatography and ultraviolet spectroscopy gave little evidence of the expected trans to cis isomerization, and provided no clues as to the composition of the brown spot. One may speculate that the degradation is due to the photochemical reactivity of the nitro group of the stilbene, but this is only conjecture. In the hope that the undesired reactivity associated with the direct irradiations might be avoided, efforts were then made to write holograms by means of the sensitized isomerization of the stilbene.

Sensitization. Biacetyl and acridine orange were selected as possible sensitizers because their singlet and triplet energies are in the appropriate range for the stilbene isomerization. The biacetyl was distilled to remove gross impurities, but was found to have minimal absorbance at 488 nm and therefore was not used. Acridine orange is insoluble in benzene and had to be added to the system dissolved in a small amount of acetonitrile. Irradiation studies of the sensitized system showed both degradation of the stilbene and changes in the absorbance of the acridine



a. Preirradiation



b. After $\frac{1}{2}$-Hour Irradiation at $\lambda > 305$ nm

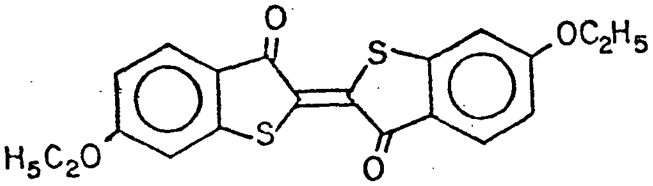
FIGURE 21. ABSORBANCE SPECTRUM OF *trans*-4-METHOXY-4'-NITROSTILBENE IN VISTANEX MM/L-120/TOLUENE GEL

1.0×10^{-4} M record at 1.0 nm/sec orange. The sensitizer apparently undergoes photochemical reactions with the polymer, or perhaps with the stilbene. Attempts to prove this by irradiation of the sensitizer alone and by chemical tests were inconclusive, and attempts to derivatize the sensitizer to a less chemically reactive form were not successful.

In view of such problems with compounds of this type, it was felt that further work with this stilbene derivative would not be productive and that other potentially useful cis-trans systems should be investigated.

Thioindigo Dyes

The first alternative cis-trans system examined was 6,6-diethoxythioindigo (compound 9). This compound was suggested as a possible candidate



9

material by the work of D. L. Ross,(13) which refers to use of this compound for the writing of relatively inefficient absorption holograms. A sample of this compound, which has been known in the open literature for a number of years, was kindly provided to us by Prof. G. M. Wyman of the University of North Carolina.

Evaluation of Holographic Recording Capability. The initial holographic experiments were carried out using compound 9 in the benzene/terpolymer gel system. As anticipated, holograms were successfully written in this system, both by trans to cis isomerization (using the 514.5 nm argon ion line) and by cis to trans isomerization (using the 457.9 nm argon ion line). Because compound 9 absorbs blue and green light rather strongly, the thioindigo/gel samples were sensitive to room light and gave a mixture of cis and trans isomers when prepared or handled under room light. The trans to cis photoisomerization of compound 9 is also thought to be strongly quenched by oxygen.(26) The samples were therefore prepared under argon, either in the dark or under red safe-lights. The desired starting isomeric composition could then be obtained simply by irradiationg the sample with an appropriately filtered xenon arc lamp; a Corning CS5-58 blue filter gave trans-rich samples, while a Corning CS3-69 cutoff filter gave cis-rich samples.

The observed diffraction efficiencies of the holograms written in the thioindigo/gel system were considerably less than those observed for the 4-methoxy-4'-nitrostilbene system. Values of ca. 0.55% were typically obtained for the thioindigo, as compared to values as high as 31% for the stilbene (see Table 1).

It was observed that under the conditions employed, the holograms could not be erased, despite the fact that they could be written both from trans to cis and from cis to trans. Unlike the stilbene, there was no evidence of chemical degradation in these samples. It is felt that the failure to erase the holograms resulted from insufficient power in the erasing beam and the fact that it requires much more energy to erase than to write a weak grating. The holograms did undergo slow, spontaneous thermal erasure over periods of several hours in the dark. This may have been due to catalysis of the (normally very slow) thermal cis to trans isomerization by acidic impurities in the system, or to the physical diffusion of isomerized molecules within the pores of the gel matrix.

Refractive Index Measurements. Attempts were made to measure the refractive index difference (Δn/mole) between the trans and cis isomers of compound 9, as had been done for the stilbene. Compound 9 is of sufficiently low solubility in benzene, however, that the refractive index of a saturated solution differed too little from that of benzene alone to permit accurate measurements using the Brice-Phoenix differential refractometer. An estimate of the effective Δn based on the diffraction efficiency data are given in Table 1.

Using the effective Δn data obtained from diffractive efficiency measurements and a knowledge of the optical energy required to produce the

TABLE 1. COMPARISON OF DATA TAKEN IN LASER/OPTICAL STUDIES OF ORGANIC SYSTEMS AND COMPARISON TO $LiNbO_3$ SYSTEM

Sample	λ Read (Write) (Å)	Absorption at λ Write (%)	$\frac{\theta}{2}$	Max. D.E.	$\frac{1}{e}$ erase $(\frac{\text{Joules}}{\text{cm}^2})$	Write Energy* for 1% D.E. (for 0.1% D.E.)	Write Power Density**	$\Delta n = \frac{2\lambda\cos}{\pi T_o}(\theta_o)\sin^{-1}(\eta^{1/2})$
4-Methoxy-4'-nitrostilbene in benzene terpolymer gel matrix	4579 (4579)	~ 61%	4.1°	31%		$2.2\ \frac{\text{joules}}{\text{cm}^2}$ $(.34\ \frac{\text{joules}}{\text{cm}^2})$	.009 W/cm^2	1.62×10^{-4}
4-Methoxy-4'-nitrostilbene in benzene terpolymer gel matrix	4579 (4579)	~ 61%	26°	0.8%			0.2 W/cm^2	2.6×10^{-5}
Trifluoro-methylbenzoyl in PMMA	6328 (6328)	22%	4.1°	.082%	20 $joules/cm^2$	$(>160\ \frac{\text{joules}}{\text{cm}^2})$	1.36 W/cm^2	1.15×10^{-5}
6-6'-Diethoxy-thioindigo terpolymer gel matrix	4579 (4579)	16%	4°	0.55%		$(14\ \frac{\text{joules}}{\text{cm}^2})$	0.65 W/cm^2	2.15×10^{-5}
0.1% Fe doped $LiNbO_3$	6328 (4880)	70%	20°	76%	113 $joules/cm^2$	$\sim .07\ \frac{\text{joules}}{\text{cm}^2}$ $(\sim .007\ \frac{\text{joules}}{\text{cm}^2})$	.044 W/cm^2	4.26×10^{-4}

* The write energy includes only that absorbed by the sample. *The energy reflected and transmitted is not included* in this table.

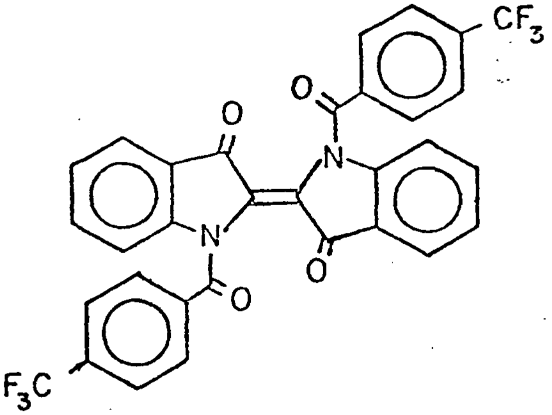
** Power density at the incident surface.

observed Δn, an effective quantum yield can be determined provided Δn/mole has been determined independently. This effective quantum yield may be significantly less than the true quantum yield as determined from the true bulk measurements. Resolution problems, molecular migration, scattering, and instabilities in the optical system used to write the diffraction grating, all can reduce the diffraction efficiency even though isomerization is occurring. Thus, the effective quantum yield and the true quantum yield may differ by several orders of magnitude.

Several unsuccessful attempts were made to incorporate compound 9 into solid polymeric matrix materials to test the claim by Ross that isomerization does occur in solid plastics. Compound 9 proved to be nearly insoluble in monomers such as styrene and methyl methacrylate, precluding the use of polystyrene and polymethylmethacrylate matrices. While the "water white epoxy" referred to by Ross(13) was not available for this work, compound 9 proved essentially insoluble in several nearly white commercial epoxy resins. Thus, while holograms were successfully written in the thioindigo/gel system, the solubility problems associated with compound 9 were so severe that it was decided to examine a more soluble material.

Indigo Dyes

The indigo dyes were a logical next choice for investigation, as their photochemistry resembles that of the thioindigos and their solubility properties are far superior. Several proprietary indigo derivatives, including N,N'-bis(4-trifluoromethylbenzoyl) indigo (compound 5), were obtained for trial evaluation.



5

These compounds proved to be far more soluble than compound 9, and were successfully incorporated in several solid matrices.

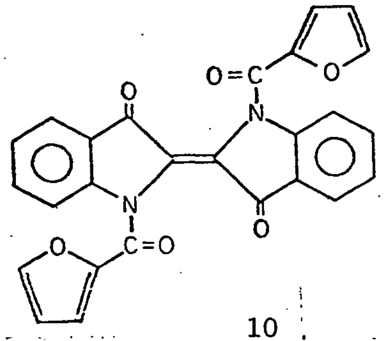
Refractive Index Measurements. As with the thioindigo compound 9, the initial holographic experiments with compound 5 were carried out in the benzene/terpolymer gel system. Holograms were readily written, as anticipated, although with somewhat less efficiency than was obtained with compound 5. Having verified that compound 5 was suitable for holography, attention was then given to measuring the refractive index properties of the compound and to incorporating it in solid matrix polymers. Solutions of compound 5 in benzene were irradiated with the filtered output of an Eimac xenon arc lamp to produce photostationary state mixtures with differing cis-trans isomeric ratios. The analysis of these mixtures, which required the calculation of the absorption spectra of the individual cis and trans isomers, has been described in the Experimental Procedure section. The refractive index of each mixture was measured relative to the benzene solvent (as for the stilbene), using the Brice-Phoenix differential refractometer. A plot of the measured refractive index values versus the concentration of cis isomer produced a straight line, the slope of which gave the value of Δn between the two isomers at the total concentration (cis plus trans) used. From this it was determined that Δn/mole for this indigo is ca. 3×10^{-3}, compared to ca. 4×10^{-2} for 4-methoxy-4'-nitrostilbene. This value of Δn/mole for the indigo is only approximate, however, because of errors introduced by the relatively low concentrations necessitated by the limited solubility of this compound.

Matrix Studies. The photorefractive behavior of the indigo derivatives in fluid solution made them attractive candidates for incorporation into solid polymers. Attempts to use epoxy resins were unsuccessful. Epon 828 epoxy resin was used, cured with amines, amides, aldehydes, and peroxides. All of the compositions tried reacted irreversibly to give a variety of highly colored products which could not be photoisomerized.

Subsequent studies, discussed in detail under Experimental Procedures, led to the successful incorporation of 5 in polymethymethacrylate. Disks of this material were then utilized to achieve the successful writing and erasing of holographic gratings, using the 632.8 nm line of a helium-neon laser for writing and the 488.0 nm argon line for erasure.

Evaluation of Holographic Recording Capability. The diffraction efficiencies achieved with these holograms were disappointingly small, ca. 0.08% (Table 1). However, the holograms obtained with compound 5 result only from the trans-cis photoisomerization of 5 and not from degradation of the system. This is clearly indicated by the reversibility of the holographic writing.

Similar results were obtained with the other indigo derivatives used, including N,N'-diacetylindigo, N,N'-dibenzoylindigo, and N,N-bis-(α-furoyl)indigo (10). In all cases, the photoisomerization proceeded cleanly and reversibly, with modest efficiencies. Significant concentration quenching was observed, with the quantum yields in fluid solution dropping more than an order of magnitude upon increasing the concentration from ca. 10^{-5} M to ca. 2×10^{-4} M. The quantum yields of photoisomerization in polystyrene or polymethylmethacrylate were roughly an order of magnitude smaller than those in fluid solution at any given concentration. No evidence for degradation was observed in any of the polymeric samples. It seems clear that, while the change in absorption spectrum induced by the trans-cis isomerization of the indigo dyes is marginally adequate for phase holographic recording (see, for instance, Figure 15), the primary cause of the low diffraction efficiencies observed is the reduction of quantum yield when the indigo is dissolved in a rigid polymeric matrix. This most likely results from the spatial requirements inherent in the trans-cis isomerization. As the indigo isomerizes, one of the bulky N-acyl substituents must sweep through an arc of roughly 180°. This is apparently severely inhibited by the polymer. It should, however,



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be possible to design polymer systems with sufficient flexibility or void space to permit the isomerization to occur with efficiencies approaching those observed in fluid solution.

Table 2 summarizes representative diffraction efficiencies measured for the full series of indigo derivatives evaluated during this program. (The efficiency reported here is defined as the ratio of first-order diffracted beam power to that in the undiffracted or zero-order beam, expressed in percent). Zero-order powers ranged from 0.8 to 2.4 mW. The first-order powers used in the calculations were the maximum values observed during the grating formation period.

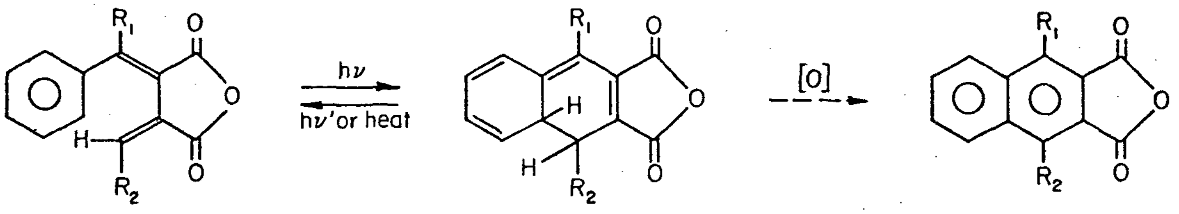
TABLE 2. DIFFRACTION EFFICIENCIES OF GRATINGS FORMED IN INDIGOID DYES IN POLYSTYRENE MATRICES

Compound	Efficiency,%
N,N'-bis-(2,4-dichlorobenzoyl)indigo	< 0.01
N,N'-bis-(5-chloro-2-nitrobenzoyl)indigo	< 0.01
N,N'-bis-(2-chlorobenzoyl)indigo	0.01
N,N'-bis-(2-chloro-5-nitrobenzoyl)indigo	0.01
N,N'-bis-(2,3,6-trichlorobenzoyl)indigo	0.01
N,N'-diacetylindigo	0.02
N,N'-bis-(4-bromobenzoyl)indigo	0.02
N,N'-bis-(3-chlorobenzoyl)indigo	0.02
N,N'-bis-(2-chloro-4-nitrobenzoyl)indigo	0.02
N,N'-bis-(3,4-dichlorobenzoyl)indigo	0.03
N,N'-bis-(2-ethoxybenzoyl)indigo	0.03
N,N'-bis-(3-trifluoromethylbenzoyl)indigo	0.03
N,N'-bis-(3-nitrobenzoyl)indigo	0.04
N,N'-dicyclohexylindigo	0.05
N,N'-bis-(2,4,6-trimethylbenzoyl)indigo	0.06
N,N'-bis-(3,5-ditrifluoromethylbenzoyl)indigo	0.07
N,N'-bis-(2,5-dimethylbenzoyl)indigo	0.08
N,N'-bis-(4-fluorobenzoyl)indigo	0.08
N,N'-bis-(3-methylbenzoyl)indigo	0.13
N,N'-bis-(2-furoyl)indigo	0.20

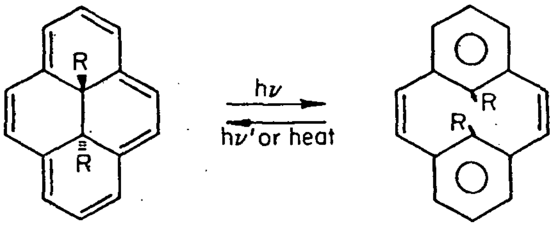
Fulgides and Dihydropyrene Derivatives

The theoretical calculations of photorefractive response as a function of wavelength shift in the absorption spectra of the isomers, as described previously, showed that the development of a successful reversible holographic recording material depends on identifying an isomer pair having absorption maxima separated by roughly 300 nm or more. Neither the stilbene derivatives nor the indigoid dyes examined fulfill this criterion. However, several classes of compounds which exhibit valence isomerization, as exemplified by certain fulgides$^{(15,21,22)}$, and derivatives of the 15,16-dialkylhydropyrenes$^{(23-25)}$, are characterized by absorption shifts from the red to the near ultraviolet upon photoisomerization.

The photoisomerization of aryl fulgides$^{(15,21,22)}$ proceeds by the process shown below in Equation 41. The presence of at least one aromatic substituent is essential, as the aromatic ring participates directly in the photoisomerization, as shown. The methine hydrogen atoms which result from the cyclization are quite reactive, and can lead to degradation and fatigue. This can be controlled, however, by the use of substituents other than hydrogen in the ortho positions of the aromatic ring and/or on the fulgide olefinic groups$^{(15,22)}$. The spectroscopic shifts observed can be quite large, depending on the choice of substituents, and the compounds retain their desirable properties sufficiently well in rigid polymer matrices that they have been considered by others for use in photochromic memories and displays$^{(15,22)}$.



The photoisomerization of the 15,16-dialkyldihydropyrenes$^{(23-25)}$, as depicted in Equation 42 is also highly attractive. It can be seen from Figure 22$^{(25)}$ that



15,16-dimethyldihydropyrene, for instance, absorbs strongly throughout much of the visible wavelength range while its photoisomer closely resembles cis-stilbene and absorbs only in the ultraviolet. The isomerization occurs clearly and reversibly both in fluid solution and in polymer matrices. It is particularly encouraging that this compound is reported$^{(24)}$ to be unaffected by oxygen and to be stable enough to be "cycled" repeatedly from one isomer to the other with no apparent degradation. Unfortunately, the quantum yields of the derivatives studied to date$^{(25)}$ are quite low (< 0.1) and the rates of thermal back-reaction are far too high (half-lives of a few hours or so) for use in a BORAM system. Both of these key properties are known to respond to substituent effects$^{(25)}$, but it is not known at this time whether they can be improved sufficiently to make this class of materials useful for incorporation in a holographic memory. This might be accomplished by a judicious combination of molecular substituent groups, polymer matrix design, and choice of separating temperature, but much research remains to be done in order to evaluate this possibility.

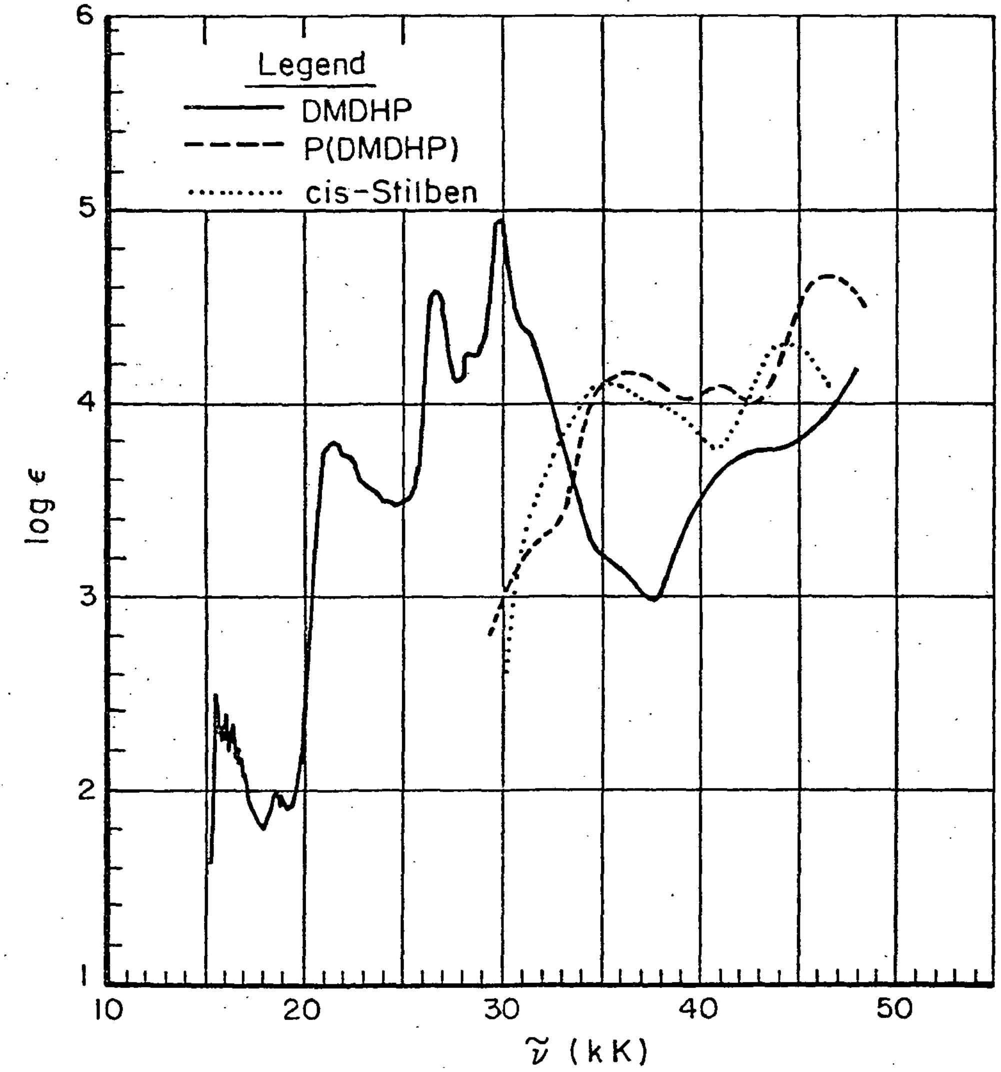


FIGURE 22. ABSORPTION SPECTRA (IN FREQUENCY UNITS), FROM REFERENCE 25: 15,16-DIMETHYLDIHYDROPYRENE (———) PHOTOISOMER OF 15,16-DIMETHYLDIHYDROPYRENE(-----) *cis* - STILBENE (·····)

Summary

Representative experimental data for the three classes of organic materials evaluated during this program are summarized below in Table 3, which includes the data for iron-doped lithium niobate for comparison. It can be seen that none of the organic materials evaluated meet the goal properties, or compare favorably to lithium niobate, for the reasons discussed above. However, these reasons are now well understood, and are readily amenable to solution by experimental means. Much research is still required to develop an operational memory, but the organic photorefractive materials offer significant potential advantages over lithium niobate by virtue of their ease of fabrication and reduced cost, and appear well worth the effort of continued development. The properties reported in the literature for the fulgides and dialkyldihydropyrenes, in particular, are sufficiently attractive to make them appealing candidates for further research.

TABLE 3. REPRESENTATIVE EXPERIMENTAL DATA

Material	η_{max}	E_{write}(FOR η = 1%
Stilbene/Gel[(a)]	31. %	220×10^{2} μJ/mm^{2}
Indigo/Polymer[(b)]	.08%	$16{,}000 \times 10^{2}$ μJ/mm^{2}
Thioindigo/Gel[(c)]	.55%	$1{,}400 \times 10^{2}$ μJ/mm^{2}
$LiNbO_3$:Fe	76. %	7×10^{2} μJ/mm^{2}
GOAL	--	0.5×10^{2} μJ/mm^{2}

(a) 4-Methoxy-4'-nitrostilbene in benzene/terpolymer gel (not reversible).

(b) N,N'-Bis-(4-trifluoromethylbenzoyl) indigo in PMMA.

(c) 6,6'-Diethoxythioindigo in benzene/terpolymer gel.

(d) 0.1% Iron-doped lithium niobate (single crystal).

CONCLUSIONS

The research performed under this contract has demonstrated the feasibility of utilizing organic photorefractive materials for reversible holographic recording. While additional research remains to be done to complete the development of a fully operational system, the problems to be solved are now both well defined and amenable to experimental resolution. The principal conclusions which may be drawn from the results of this program are as follows:

- The development of a reversible, high-capacity, holographic optical memory based on the photochemical isomerization of organic materials now appears to be feasible.
- The utilization of organic photorefractive materials in such a system will almost certainly lead to significant benefits in lower fabrication cost and much greater flexibility of design as compared to lithium niobate or other inorganic materials which must be fabricated as single crystals. This is because the organic materials can be simply dissolved in an appropriate polymeric matrix and then formed into any shape desired.
- A theoretical analysis of the changes in refractive index and in absorption spectrum required for a "goal case" recording material has demonstrated that the absorption spectrum of the material must shift from the visible region into the near ultraviolet upon isomerization.
- Because of the limited shifts of their absorption spectra and their problems with photodegradation, the stilbene derivatives examined during this program appear to be unsuitable for reversible holographic recording.
- On the basis of the above criteria, the indigoid dyes evaluated are marginally adequate for use in a holographic memory. These compounds presently do not exhibit the required sensitivity, because of concentration quenching and because the matrix materials used to date inhibit the isomerization.

- The 15,16-dialkyldihydropyrenes and fulgides appear to have nearly ideal spectroscopic properties, and are not significantly perturbed by incorporation in a polymer matrix. The rate of thermal back-reaction (spontaneous erasure) is too rapid for many of these compounds, but this may be solvable by structural modification of the compounds.
- The optical problems inherent in the system requirements are severe, but can be overcome. While it does not seem feasible to attempt the use of different wavelengths for writing and reading, the undesired erasure incurred by using a single wavelength for both reading and writing can be minimized by the use of low power levels for reading.
- In summary, a satisfactory, reversible, holographic recording material, while not yet optimized, has been defined in principle. This is an accomplishment which could ultimately lead to the development of a totally new generation of optical memories.

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