process used to the syntheses of pseudopelletierine,[56] mp 65°. This substance formed a picrate in methanol, which melted at 270°. *Anal.* Calcd for $C_{11}H_{19}NO$, $C_6H_3N_3O_7$: C, 49.75; H, 5.40; N, 13.65; O, 31.39. Found: C, 49.89; H, 5.32; N, 13.46; O, 31.33. The infrared spectrum of 11 shows characteristic peaks at 3250 cm^{-1} (N–H) and 1720 (cm^{-1} (C=O); nmr (CD$_2$Cl$_2$) δ 1.2 ppm (6 H), multiplet 2.2 (4 H), 0.85 ppm (4 H).

1,5,7-Trimethylnorpseudopelletierine N-Oxyl, 12. To a solution of 1 g of 1,5,7-trimethylnorpseudopelletierine in 10 ml of water was added 10 mg of phosphotungstic acid and 1.2 ml of hydrogen peroxide. The reaction mixture was cooled in an ice bath. After

(56) A. C. Cope, H. L. Bryden, Jr., and C. F. Howell, *Org. Syn.*, 4, 816 (1963).

stirring for 2 hr, the mixture was extracted by methylene chloride. The solvent was removed and yielded 1 g of crude product which was then purified by chromatography on alumina.

We obtained 530 mg of pure radical (50% yield), mp 74°, esr spectrum in dilute solution in methylene chloride a_N = 18 G. *Anal.* Calcd for $C_{11}H_{18}NO_2$: C, 67.31; H, 9.24; N, 7.14; O, 16.30. Found: C, 67.34; H, 9.35; N, 7.35. The infrared spectrum shows no band in the absorption region 3250 cm^{-1} (N–H).

Spectroscopic Studies of Some Laser Dyes

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Abstract: The chief parameters determining laser action of organic dyes are introduced. Favorable constellations in a chromophore are discussed which are necessary to convert it into a potential laser dye; that is, an auxochromic-group-substituted compound showing only small triplet–triplet (T–T) absorption over its fluorescence region. T–T laser photoselection spectroscopy is shown to be a valuable tool for obtaining polarization data on T–T absorption bands. The S–S absorption, fluorescence, and T–T absorption and polarization spectra of p-terphenyl, p-quaterphenyl, PPO, BBO, POPOP, and α-NPO were measured. T–T absorption and polarization spectra of some of these indicates that an improvement in laser action should occur when they are para-substituted by auxochromes. p,p'-Diamino- and p,p'-N,N,N',N'-tetraethyldiaminoterphenyl, p,p'-diamino- and p,p'-N,N,N',N'-tetraethyldiaminoquaterphenyl, and p,p'-dibutoxy-POPOP were synthesized. Their T–T absorption showed remarkably large red shifts; moreover, the bands for the aminooligophenylenes were very broad. This indicates nonplanarity of higher triplet states. Out-of-plane molecular electronic states reduce quantum fluorescence yield. To improve laser performance, ways to render the molecule coplanar are presented. Commercially available laser dyes are classified according to their constellations, and some of their spectroscopic data are presented. It is concluded that dyes with far better laser action properties could be synthesized. Some suggestions are made as to which chromophores appear most promising for conversion into potential laser dyes.

O rganic compounds (laser dyes) showing laser action under flashlamp excitation can be divided into two classes.

A. Compounds belonging to the classical organic dyes, like rhodamine 6G, fluorescein, seven-position substituted coumarin, and others[2a] make up the first class. In these molecules, benzene rings (or its heterocyclic derivatives) are positioned adjacent to each other, as in naphthalene, anthracene, acridine, etc. According to dyestuff theory, an organic dye is formed by the substitution of a hydrogen atom(s) in a chromophore (parent aromatic compound) by a so-called auxochromic group(s) like R$_2$N, RHN, H$_2$N, HO, and RO. The fluorescence region (laser action region) of these compounds stretches from the violet to the near-infrared region. Chromophores have in general rather low (or sometimes zero) quantum fluorescence yield ϕ_F. Many of the classical dyes have a ϕ_F close to unity.

B. Laser action under flashlamp excitation has also been reported in the so-called organic scintillators.[2a] Remarkably, these compounds are not organic dyes in the classical sense, since they contain no auxochromic groups. The spectral region of these compounds extends from the near ultraviolet (p-terphenyl at about 3400 Å) to the blue. Although containing no auxochromic groups, many of the organic scintillators have a ϕ_F close to unity.[2b]

Organic scintillators, for reasons which will become apparent later, should actually be subdivided into two subgroups. (a) The first is chain-type molecules. They are either phenyl rings joined together by single carbon–carbon bonds (*e.g.*, p-terphenyl) or five-membered rings like oxazole, joined to phenyl rings, like POPOP (2,2'-p-phenylenebis(5-phenyloxazole)), BBO (2,5-di(4-biphenylyl)oxazole), and others.[2a] (b) The second is combinations of groups belonging to class B with chromophores belonging to class A, like α-NPO (2-(1-naphthyl)-5-phenyloxazole).[2a]

One can to some extent predict the amount of T–T absorption present over the fluorescence region of an organic dye from the polarization characteristics of its lowest energy S–S absorption band(s) and T–T absorption band(s) located in or near the fluorescence

region of its chromophore, from the nature of the substituent group, and from the group location.[3]

For obtaining new and possibly better laser dyes, there are only two main constellations, where substitution by auxochromic group(s) will yield a potential laser dye, that is, a compound which has only small T–T absorption over the fluorescence region. If, in addition, the substitution yields a compound with a ϕ_F close to unity, then, in the respect at least, a new laser dye will have been synthesized.

So that the present paper can be followed more easily, we present an abbreviated version of the term constellation. This term refers to a particular relative disposition in wavelength of several electronic transitions (S–S, fluorescence, and T–T), including their relative polarizations and intensities of chromophores and dye molecules. In Figure 1 we show the two main (A_2a and B_1a) and the two subordinate ($A_2'a$ and $B_1'a$) constellations needed in a chromophore so there will be small (A_2c and $A_2'c$) or no (B_1c and $B_1'c$) T–T absorption present in the substituted compound (the potential dye laser material).

We assume that there is at least one T–T absorption band present at the long-wavelength side (fluorescence region) of the $S_0 \rightarrow S_1$ absorption band of a chromophore (an aromatic compound or its heterocyclic derivative). In a symmetric chromophore, all S–S and all T–T absorption bands are polarized (have their corresponding oscillator positioned) along either the short or the long molecular axis only π,π^* transitions are considered. Following substitution of a hydrogen atom by an auxochromic group, for example, at the short molecular axis, all short-axis polarized S–S absorption bands are red shifted and intensified. All short-axis polarized T–T absorption bands, however, are much more red shifted than the S–S absorption bands. The long-axis polarized S–S and T–T absorption bands are more or less unaffected by the short-axis substitution. A long-axis substitution would affect the long-axis polarized S–S and T–T absorption bands in the same manner, leaving the short-axis polarized S–S and T–T absorption bands unaffected.

1. In a chromophore with an A_2a constellation, the further the T–T absorption band is positioned to the red side of the $S_0 \rightarrow S_1$ band the better. The two bands are similarly polarized. Substitution by an auxochromic group in the direction of the two oscillators moves the $S_0 \rightarrow S_1$ and (very much) the T–T absorption band to longer wavelengths. The large red shift of the T–T absorption band is very desirable. However, the red shift of the $S_0 \rightarrow S_1$ absorption band also causes the fluorescence spectrum to move to longer wavelengths, reducing somewhat the desired large red shift of the T–T absorption band.

If originally in the A_2a constellation the T–T absorption band is positioned closer to the $S_0 \rightarrow S_1$ absorption band, its red shift following substitution will leave considerable T–T absorption in the fluorescence region, which might prevent laser action altogether.

2. The $A_2'a$ constellation is to be preferred over the straight A_2a. Here, the $S_0 \rightarrow S_1$ absorption band is polarized perpendicularly to the T–T absorption band. The T–T oscillator, however, is positioned parallel to the $S_0 \rightarrow S_2$ oscillator. Substitution in the direction of the $S_0 \rightarrow S_2$ oscillator must move the corresponding absorp-

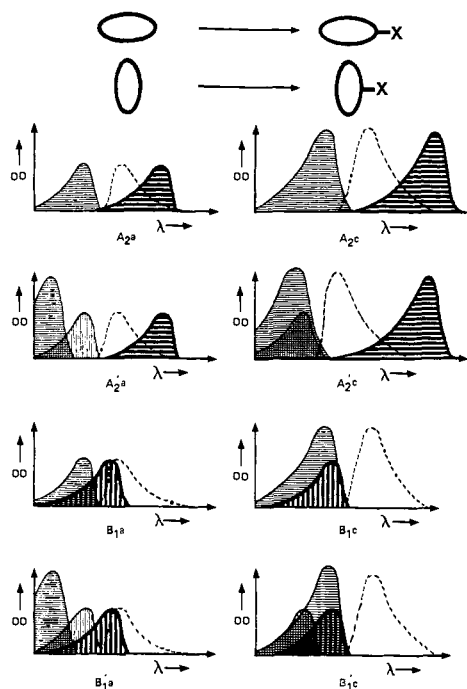(3) T. G. Pavlopoulos, *IEEE J. Quantum Electron.*, 9, 510 (1973).

Figure 1. Substitution effects by an auxochromic group (X) on the electronic spectrum (graph) of a chromophore (left side, starting constellation) which convert it into a potential organic dye laser material (right side, ending constellation). The S–S absorption spectrum on the left side of each graph is represented by one or two narrow-line curves and the T–T absorption band on the right side by a heavy curve. The directions of their corresponding absorbing oscillators (S–S and T–T) within the molecule are indicated by the directions of the shading (horizontal or vertical lines). The fluorescence spectrum in each graph is mirror symmetric to the $S_0 \rightarrow S_1$ absorption band and is shown as a dashed curve. The shape of a molecule is approximated by an ellipse appearing above the graphs. The molecule on the top, in which the long axis is horizontally positioned, would have in its starting A_2a constellation the $S_0 \rightarrow S_1$ and the T–T absorbing oscillators positioned along the long axis of the molecule. The effects of long-axis substitution are shown in the ending constellation A_2c, a potential laser dye. Another molecule is represented in the figure with its short axis horizontally arranged. Substitution is performed along the short axis. The resulting constellations were not presented in ref 3. The starting constellations correspond to: $D_2a \leftrightarrow A_2a$, $D_2'a \leftrightarrow A_2'a$, $C_1a \leftrightarrow B_1a$, and $C_1'a \leftrightarrow B_1'a$. The ending constellations correspond to: $D_2b \leftrightarrow A_2c$, $D_2'b \leftrightarrow A_2'c \leftrightarrow B_1c$, and $C_1'b \leftrightarrow B_1'c$.

tion band sufficiently to the red until it has about the same energy as the $S_0 \rightarrow S_1$ band. The spectral location of the fluorescence spectrum will remain about the same. Therefore, an $A_2'a$ constellation should generally yield less T–T absorption over the fluorescence region than a straight A_2a constellation.

3. The B_1a constellation is the most attractive one. Ideally, there should be no T–T absorption present to the red side of the T–T absorption band, which is rather closely positioned to the $S_0 \rightarrow S_1$ absorption band. The bands are polarized perpendicularly to each other and substitution again is performed in the direction of the $S_0 \rightarrow S_1$ oscillator. The resulting red shift of this band simply moves it over the unaffected T–T absorption band and the fluorescence spectrum falls into a region with no T–T absorption present.

4. The $B_1'a$ constellation is a combination of the $A_2'a$ and B_1a. Following substitution in the direction of the $S_0 \rightarrow S_2$ oscillator, the resulting red shift of this band must be sufficiently large to overtake not only the

perpendicularly polarized $S_0 \rightarrow S_1$ band but also the T–T absorption band.

As mentioned above, some organic scintillators already show laser action under flashlamp excitation. Two important problems, which prompted this investigation, arise. (1) Chemically, the organic scintillators can be considered as chromophores. Therefore, an investigation of their T–T absorption polarization spectra should be of considerable interest. Some of them may possess one of the proper constellations. Substitution by auxochromic group(s) could possibly convert them into more efficient laser dyes. (2) It is rather well established that substitution by auxochromic groups in chromophores will intensify (hyperchromic effect) and red shift (bathochromic effect) all those S–S absorption bands which are polarized (resulting from an oscillator which is oriented) in the direction of the substituent.[4] T–T polarization experiments on coumarin and 7-hydroxy- and 7-diethylamino-4-methylcoumarin indicate that a similar, but much stronger, effect is observable with regard to T–T absorption bands.[3] These large red shifts of T–T absorption bands following substitution by auxochromic groups are crucial in determining laser action properties of organic dyes. It would be desirable to establish that this effect, which has been observed only on T–T absorption bands of coumarin, is of general nature.

The measurement of S–S and T–T absorption and polarization spectra and the fluorescence spectra of some organic scintillators and some of their substituents would answer some of the questions raised above.

For flashlamp pumped laser dyes, losses from the product

$$L = n_{T_1} \epsilon_T(\lambda_F) D \qquad (1)$$

are the most serious. n_{T_1} is the concentration of molecules in the lowest triplet state T_1 and $\epsilon_T(\lambda_F)$ is the molar triplet extinction coefficient in the spectral region of laser action.

These triplet state molecules are produced by the excitation flash. Even in very small concentrations, they act as very efficient absorbers, since they have been produced within the laser cavity. When laser action takes place, the laser beam is reflected back and forth between the two mirrors of the laser cavity many, many times, resulting in a very large path length D.

For $\phi_F = 1$, one would have $n_{T_1} = 0$. However, due to spin–orbit coupling, always $n_{T_1} \neq 0$ and consequently always $\phi_F < 1$. It should, therefore, be noted that even compounds with ϕ_F very close to unity, but with a large ϵ_T over the fluorescence region, will not exhibit any laser action under flashlamp excitation. For example, 9,10-diphenylanthracene has a ϕ_F very close to unity[2b] but a rather large triplet extinction coefficient over the fluorescence region.[5] This compound not only does not show any laser action under flashlamp excitation[6] but has a rather large laser action threshold under nitrogen laser excitation.[7]

For efficient laser action, the product $n_{T_1} \epsilon_T(\lambda_F)$ must be kept very small. A ϕ_F very close to unity is one of

the most important requirements, since for $\phi_F \rightarrow 1$, $n_{T_1} \rightarrow 0$. Equally important, the molar triplet extinction coefficient $\epsilon_T(\lambda_F)$ reaching into the fluorescence region must be very small (ideally zero).

The effect of substituents on the $\epsilon_T(\lambda)$, and to some extent on n_{T_1}, is the main topic of this article. Although suitable triplet state quenchers reduce n_{T_1}, they also quench the fluorescence at higher quencher concentrations. Therefore, a substantial lowering of ϵ_T at the spectral region of laser action should have a large effect on lowering the laser action threshold and increasing the dye laser efficiency. Another possible area of laser dye research is to minimize the intersystem crossing rates.

The selection of organic scintillators for this study was based on the following criteria. (1) The compound must be representative of its group. (2) As excitation source, the 3250-Å line from a continuous wave Cd–He laser was available. Therefore, only molecules which absorb this line strongly could be studied. (3) The phosphorescence lifetime τ_P must be sufficiently long to permit the accumulation of sufficient triplet state molecules. (For example, the τ_P of p-bis(o-methylstyryl)benzene (bis-MSB) was too short to detect any triplet absorption.) (4) The study required that a solvent be found which forms a glass at liquid nitrogen temperature and in which photochemical reactions are small.

Experimental Section

A. The Spectroscopic Arrangement. The experimental setup used to measure the T–T absorption and polarization spectra has been presented elsewhere.[8] In all experiments, the 3250-Å line from a continuous wave Cd–He laser (Model 185, Spectra Physics) was employed for excitation.

The T–T absorption spectra are presented in terms of triplet optical densities OD_T, defined in the usual way

$$OD_T \equiv \log I_T^0/I_T = \epsilon_T n_{T_1} d \qquad (2)$$

where ϵ_T is the molar triplet extinction coefficient, n_{T_1} the molar concentration of triplet state molecules, and d the thickness of the sample.

It can be assumed that the number of triplet state molecules produced was different for every compound investigated. The OD_T curves, therefore, cannot be used to compare T–T absorption of the different compounds. This is only possible if one presents $\epsilon_T = f(\lambda)$. In principle, it is possible to obtain rather accurate values of $\epsilon_T(\lambda)$ by employing continuous wave laser excitation.[9] However, two criteria must be fulfilled for using this method efficiently. (1) The excitation must fall into a region of strong S–S absorption, to ensure a high degree of depletion of the ground singlet state molecules. (2) The spectral region where the effect of depletion is measured must also be a region of strong S–S absorption but must not be located too close to the spectral region of excitation. Otherwise, unabsorbed excitation light will saturate the photomultiplier and make exact measurements impossible.[9]

Conditions 1 and 2 were not met by most of the molecules investigated in this work, because only the 3250-Å continuous wave laser line was available for excitation. (This can be seen from their S–S absorption spectra shown in Figures 4–14.)

The fluorescence spectra of the different compounds were also measured with the same spectroscopic equipment. The photomultiplier output was connected directly to the recorder, bypassing the lock-in amplifier.

We would like to emphasize that T–T laser photoselection spectroscopy[10,11] is a very suitable method for spectroscopic studies related to laser dye structure. Absolute polarization measurements,

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that is, the determination of the direction of the S–S and T–T absorbing oscillators within the molecular frame, are experimentally difficult. Relative polarization measurements employing photoselection spectroscopy,[12] however, are experimentally simple.

In T–T photoselection spectroscopy the degree of polarization P is defined by

$$P = \frac{3 \cos^2 \theta - 1}{\cos^2 \theta + 3} = \frac{OD_{\parallel} - OD_{\perp}}{OD_{\parallel} + OD_{\perp}} = \frac{\epsilon_T^{\parallel} - \epsilon_T^{\perp}}{\epsilon_T^{\parallel} + \epsilon_T^{\perp}} \quad (3)$$

$OD_{\parallel}$ and $OD_{\perp}$ are the parallel and perpendicular T–T optical densities.[12] *From the degree of polarization P one can determine the angle θ between the absorbing S–S oscillator and the T–T oscillators.* If the two oscillators are parallel to each other ($\theta = 0°$), then $P = \frac{1}{2}$; if they are perpendicular ($\theta = 90°$), then $P = -\frac{1}{3}$. These two cases, however, present limits which in practice are merely approached.

If one excites into the lowest energy S–S absorption band of a chromophore, a positive degree of polarization P of a T–T absorption band indicates the presence of an $A_2a(D_2a)$ constellation. A negative P indicates a $B_1a(C_1a)$ constellation. The knowledge of P (that is, of θ) alone is not sufficient to determine the absolute orientation of the oscillators within the molecular frame. However, in many cases, the direction of the lowest energy S–S or a T–T oscillator within the molecular frame is known, or can be deduced from similarly constructed molecules. Measuring P, one can then determine the direction of the T–T oscillators in the first case and the direction of the S–S oscillator into which the excitation took place in the second case.

The S–S absorption spectra were recorded with a Cary spectrophotometer. Due to lack of proper equipment, no quantum fluorescence yields ϕ_F of the substituted compounds could be measured. Nor was a dye laser system with a very fast rise time flashlamp available, to demonstrate laser action in the five substituted organic scintillators. However, all these compounds showed strong laser action under nitrogen laser excitation. These compounds could be termed good dyes. As an indication of the present state of the art, manufacturers of commercial nitrogen dye laser combinations quote pulse repetition rates to 10 Hz for nonflowing dye solutions. The present materials lased up to 100 Hz in static systems.

These experiments were carried out with an AVCO Everett C950 and C5000 pulsed nitrogen laser–dye laser combination.

B. Chemicals. Sources of the organic scintillators: *p-terphenyl* from Princeton Organics (Par Grade), $1 \times 10^{-2} M$ solution in tetrahydro-2-methylfuran from Analabs (Chromat Grade); *p-quaterphenyl* from James Hinton (SHGR Grade), $1 \times 10^{-3} M$ solution in tetrahydro-2-methylfuran: *2,5-diphenyloxazole (PPO)* from Aldrich Chemical Co. (Scintillation Grade), $2 \times 10^{-3} M$ solution in EPA from American Instrument Co.; *2,5-di(4-biphenylyl)oxazole (BBO)* from Sigma Chemical Co. (was zone refined, over 25 passes), $2 \times 10^{-3} M$ solution in tetrahydro-2-methylfuran; *1,4-bis(5-p-n-phenyloxazol-2-yl)benzene (POPOP)* from Eastman (Scintillation Grade), $2 \times 10^{-3} M$ solution in tetrahydro-2-methylfuran; *2-(1-naphthyl)-5-phenyloxazole (α-NPO)* from Eastman (Scintillation Grade), $1 \times 10^{-3} M$ solution in 3-methylpentane from Analabs (Chromat Grade).

The substituted terphenyl and *quaterphenyl* dyes were made according to Figure 2. The first nitration steps were improvements over existing literature methods of making the *p,p'*-dinitropolyphenyls,[13,14] and all steps were monitored by nuclear magnetic resonance spectroscopy. Alkylation of the diamines by reaction in refluxing trialkyl phosphates[15] was found to be an effective method for making the *N,N,N',N'*-tetraethyldiamines. Melting behavior suggestive of liquid crystal properties was observed for dinitroquaterphenyl.

The nuclear magnetic resonance (nmr) spectrum for *p,p'-dinitroterphenyl* in hot dimethyl sulfoxide appeared as an aromatic singlet superimposed on an A_2B_2 quartet so as to obscure the high field peak of the quartet.

For *p,p'-diaminoterphenyl*, the nmr spectrum in dimethyl sulfoxide (A-60) included a singlet at 7.69 downfield of an A_2B_2 quartet at 7.61, 7.48, 6.88, and 6.77 with a ratio of integrated intensities being 1:2. The nmr spectrum of *p,p'-tetraethyldiaminoterphenyl* (A-60) in deuteriochloroform showed the ethyl triplet and quartet centered at
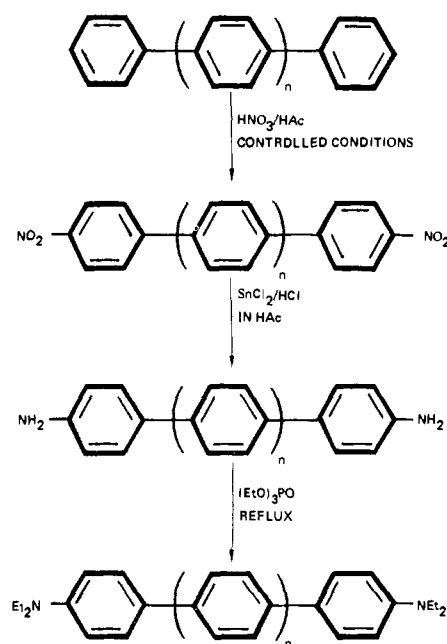
Figure 2. Synthesis of *p,p'*-diaminoterphenyl ($n = 1$) and quaterphenyl ($n = 2$) and their *N,N,N',N'*-tetraethyl derivatives.

1.20 and 3.42, respectively, and the aromatic protons which appeared as a singlet 7.62 superimposed an A_2B_2 quartet at 7.49, 6.87, and 6.72, so as to obscure the low field peak of the quartet. Integrated intensities were in accord with the supposed structure.

The time averaged nmr spectrum of *p,p'-dinitroquaterphenyl* in hot dimethyl sulfoxide appeared as a singlet superimposed on an A_2B_2 quartet with the singlet covering the high field peak of the quartet.

For *p,p'-diaminoquaterphenyl*, the nmr spectrum (A-60) in dimethyl sulfoxide included an aromatic singlet 7.52 to low field of an A_2B_2 quartet 7.37, 7.22, 6.59, and 6.44 with integrated intensities in the ratio 1:1.

The nmr spectrum of *p,p'-tetraethyldiaminoquaterphenyl* (A-60) in deuteriochloroform showed the ethyl triplet and quartet centered at 1.22 and 3.46, whereas the aromatic signals appeared as a singlet 7.71 superimposed on an A_2B_2 quartet 7.53, 6.89, and 6.75, so as to obscure the low field peak. Integrated intensities were in accord with the proposed structure.

A $1 \times 10^{-3} M$ solution of *p,p'-diaminoterphenyl* and $5 \times 10^{-4} M$ solutions of *p,p'-tetraethyldiaminoterphenyl*, *p,p'-diaminoquaterphenyl*, and *p,p'-tetraethyldiaminoquaterphenyl* in tetrahydro-2-methylfuran were employed in the experiments.

1,4-Bis(5-p-n-butoxyphenyloxazol-2-yl)benzene (*p,p'-dibutoxy-POPOP*) was prepared according to the method outlined in Figure 3, for the most part following customary procedures.[16–19] The rationalization was that (a) two alkoxy substituents on a POPOP dye should shift the fluorescence into the blue-green; (b) the alkoxy group as an auxochrome should be superior to the amino, in that it does not introduce the weak C–N single bond; and (c) butoxy groups should help solubilize the dye in organic solvents. The last modification made the earlier materials in the synthesis difficult to handle, whereas the later stages were amenable.

A $1 \times 10^{-3} M$ solution of *p,p'-dibutoxy-POPOP* in tetrahydro-2-methylfuran was used.

Results

p-Terphenyl.[6] Biphenyl possesses a broad S–S absorption band, with its maximum located at about 2600 Å.[2b] It shifts to about 2750 Å for *p*-terphenyl and to 2900 Å for *p*-quaterphenyl.[2b] In all these compounds, the oscillator belonging to the strong S–S ab-

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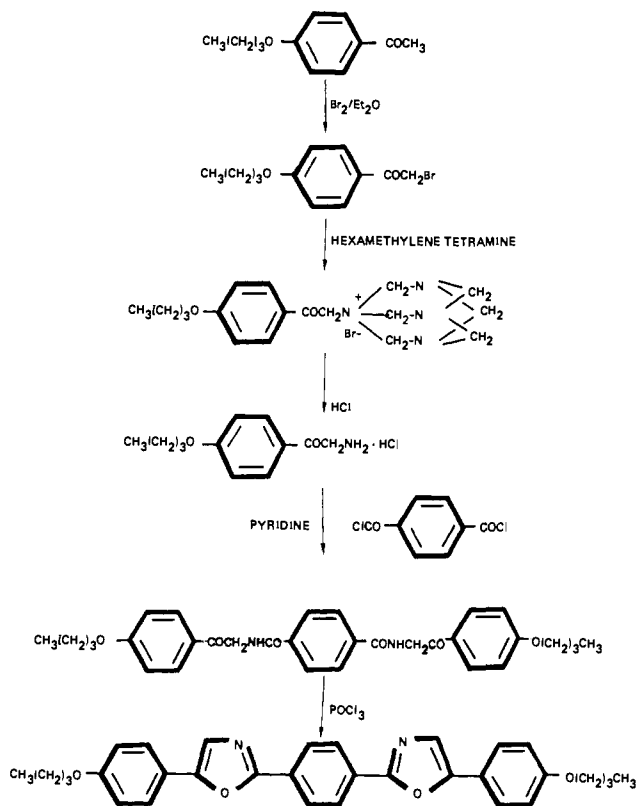
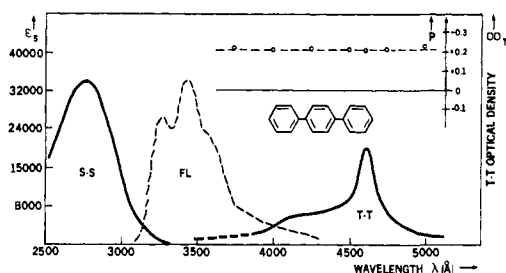**Figure 3.** Synthesis of 1,4-bis(5-*p*-*n*-butoxyphenyloxazol-2-yl)-benzene (dibutoxy-POPOP).

Figure 4. S–S and T–T absorption spectrum of *p*-terphenyl in tetrahydro-2-methylfuran at 77°K. The degree of polarization *P* is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.

sorption band is located along the long axis of the molecule. Two differently polarized transitions are hidden at the long-wavelength side.[20,21]

A strong T–T absorption band is located at about 3600 Å in biphenyl.[22] In *p*-terphenyl the fluorescence maximum is located at about 3400 Å.[2b] Due to long-axis substitution in the para position in biphenyl by another phenyl group (*i.e.*, *p*-terphenyl), the maximum of the T–T absorption band has moved to about 4600 Å.[22] Therefore, one can expect that only the weak tail of this strong T–T band will overlap with the fluorescence (laser action) region. $\phi_F = 0.93$[2b] and the compound shows remarkable laser action properties (super-radiance) when flashlamp pumped.[6]

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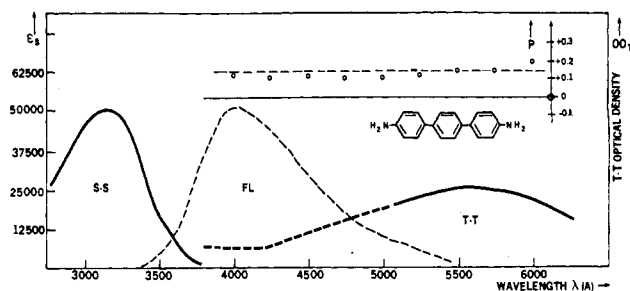
Figure 5. S–S and T–T absorption spectrum of *p,p'*-diaminoterphenyl in tetrahydro-2-methylfuran at 77°K. The degree of polarization *P* is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.
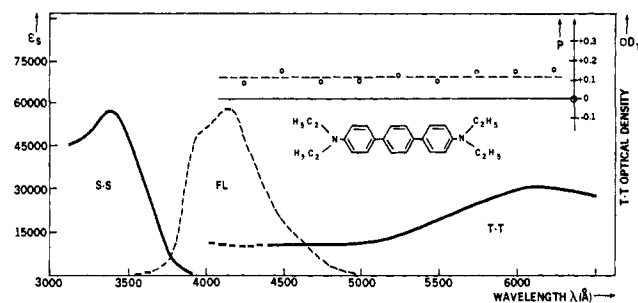

Figure 6. S–S and T–T absorption spectrum of *p,p'*-tetraethyl-diaminoterphenyl in tetrahydro-2-methylfuran at 77°K. The degree of polarization *P* is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.

The S–S absorption, fluorescence, and T–T absorption and polarization spectrum of *p*-terphenyl are presented in Figure 4. The 3250-Å continuous wave line employed for excitation most likely falls into the onset of the strong, long-axis-polarized S–S absorption band. Since the strong T–T absorption band at 4600 Å[22] should also be long-axis polarized, we observe a correct positive degree of polarization *P*. Although this result might have been expected, there is an important observation to be made. *p*-Terphenyl presents a chromophore *possessing an A_2a constellation*. The strong S–S and the strong T–T absorption bands are separated by a large energy gap of about 2000 Å. Long-axis substitution, for example, in the *p,p'* positions by two amino or diethylamino groups should very much red shift the strong T–T absorption band from the blue spectral region to the orange or even red spectral region.

The S–S absorption, fluorescence, and T–T absorption and polarization spectrum of *p,p'*-diaminoterphenyl and *p,p'*-tetraethyldiaminoterphenyl are presented in Figures 5 and 6, respectively.

The introduction of the two amino groups in the para position of *p*-terphenyl has red shifted the maximum of the strong T–T absorption band about 1000 and about 1500 Å by the two amino groups or diethylamino groups, respectively.

We have also measured the degree of polarization *P* of all the substituted compounds. As expected, *P* remains positive in all cases studied.

Besides the large red shift of the maximum of the T–T absorption band in substituted compounds, their exceptional broadness is their most remarkable feature. The "smearing out" of the T–T absorption bands runs counter to our original aim, to reduce T–T absorption

over the fluorescence region in the substituted compounds. The broad T–T absorption spectra indicate that the molecules in their triplet state are not planar. This effect will be further amplified upon in the discussion section.

All the compounds studied showed some photodecomposition, especially in the near ultraviolet–violet region.[23] All the amino and diethylamino compounds decomposed rather strongly, especially in the violet–blue spectral region. Especially unstable was p,p'-diaminoterphenyl.

Regions of reduced measurement accuracy in the T–T absorption curves are presented by a dashed contour. The reduced measurement accuracy resulted from the weakness of the T–T absorption, from photodecomposition, or from both.

It further seems that a second T–T absorption band has appeared at the short-wavelength side of the fluorescence spectrum. Originally, this band might have been located in the ultraviolet S–S absorption region of p-terphenyl. It has been red shifted following substitution.

p-**Quaterphenyl.**[6] Adding another phenyl group at the p position in terphenyl moves the S–S absorption spectrum to about 2950 Å and the fluorescence spectrum maximum to about 3600 Å. Again, the T–T absorption maximum experiences a large red shift to about 5300 Å due to long-axis substitution. As is apparent from Figure 7, only little T–T absorption intensity is present over the fluorescence region. This fact, together with the large Stokes shift and the rather high ϕ_F = 0.89 explains why this compound shows laser action under flashlamp excitation. p-Quaterphenyl does not lase as efficiently as p-terphenyl[6] because of higher T–T absorption over the fluorescence region. This is probably the dominant effect since the ϕ_F are so similar (0.89 $vs.$ 0.93).

There is a dip in the polarization curve P at and near the very strong 0,0 band of p-quaterphenyl. When the compound was excited with radiation of lower intensity, the P values (presented as dots in Figure 7) approached the values of the neighboring ones. The degree of polarization P of p-quaterphenyl is positive. Because the strong T–T absorption band in the green spectral region is long-axis polarized excitation into the 3250-Å region indicates the presence of a long-axis-polarized S–S absorption band in this region. Therefore, also in p-quaterphenyl, we have an A_2a constellation present.

The spectra for p,p'-amino- and p,p'-diethylaminoquaterphenyl are shown in Figures 8 and 9, respectively. They are very similar to those corresponding to the p-terphenyl derivatives shown in Figures 5 and 6. The T–T absorption maximum in p,p'-amino- and p,p'-
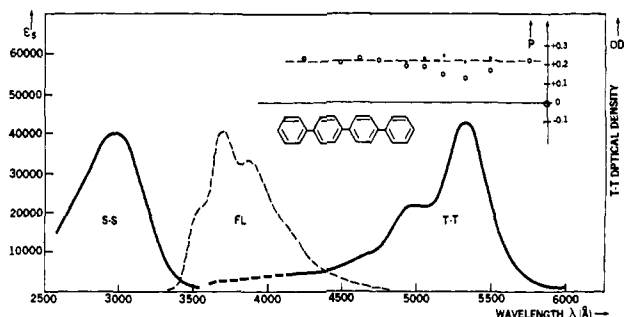

Figure 7. S–S and T–T absorption spectrum of p-quaterphenyl in tetrahydro-2-methylfuran at 77 °K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.

diethylaminoquaterphenyl has been red shifted about 1200 and 1800 Å, respectively.

Also, in these two compounds, a second T–T absorption band seems to make its appearance. Its maximum is probably covered by the S–S absorption band, and only its onset reaches into the fluorescence region.

The diamines and the tetraalkyldiamines lased well on the nitrogen laser. The quaterphenyls verged on the edge of the blue-green region in polar solvents such as dimethyl sulfoxide, although the strongest response was in the blue, whereas the terphenyls went as far as the violet. These dyes have the following drawbacks. They are of high molecular weight and require long-chain alkyl groups to make them sufficiently soluble in organic solvents, and solution in water also necessitates much chemical modification. Use of two strong auxochromic groups, NR_2, diminishes the ionization potential of the molecule so that direct or photochemical oxidation becomes a problem.[24]

Diphenyloxazole (PPO).[6] Oxazole, like the other five-membered ring-type heterocyclic compounds, has aromatic character. Therefore, to explain its absorption spectra, one may speculate along the following lines. The T–T absorption spectrum of PPO should roughly resemble that of p-terphenyl. It should be located in the blue-green region and should be long-axis polarized. Experimentally, we observe the maximum of the T–T absorption spectrum at about 5100 Å, exhibiting $positive\ polarization$ (see Figure 10). The S–S absorption maximum is located at 3100 Å and must therefore be polarized along the long axis of the molecule. This long-axis polarization may be explained the following way. Placing an oxazole group between two phenyl groups could have red shifted the long-axis-polarized transition, which is strong and was located in the 2750-Å region of p-terphenyl. Experimental results to support these assumptions will be furnished in the section on dibutoxy-POPOP. One would also have an A_2a constellation in PPO. Long-axis substitution by an auxochromic group(s) then could also improve laser action of this compound. No attempt was made to synthesize derivatives.

2,5-Di(4-biphenylyl)oxazole (BBO).[6] Following the reasoning applied to the S–S and T–T absorption spectra of PPO, one would also have an A_2a constella-

(23) To reduce errors resulting from photodecomposition and absorption from photodecomposition products, the following method was employed. First, the measurements were performed at discrete wavelengths. Second, the liquid nitrogen dewar which contained the sample was placed on top of a lab jack. To measure the OD_T's, $I^0(\lambda_1)$ was recorded, followed by $I_T(\lambda_1)$. After the excitation source (the continuous Cd–He laser) was cut off, and the lab jack was lifted somewhat, until the recorder showed $I^0(\lambda_1)$ again. Then the monochromator grating was set at λ_2 and $I^0(\lambda_2)$ was recorded, etc. For measuring P, a similar procedure was adopted. $I_{\parallel}^0(\lambda_1)$ and $I_{\parallel}(\lambda_1)$ were first recorded. Then, after cutting off the excitation source, the lab jack was lifted until $I_{\parallel}^0(\lambda_1)$ was recorded on the recorder. The analyzer was turned 90° to the perpendicular position, yielding $I^0_\perp(\lambda_1)$ and $I_\perp(\lambda_1)$. The lab jack was lifted again until $I^0_\perp(\lambda_1)$ was obtained. The monochromator grating was set for λ_2 and the procedure was repeated for $I_\perp{}^0(\lambda_2)$, etc.

(24) Substitution of a phenoxide anion group in place of the terminal aniline should produce molecules having similar spectral properties together with water solubility: P. R. Hammond, "Blue-Green Lasing Dyes," Naval Weapons Center, Technical Publication, NWC TP 5562, September 1973.
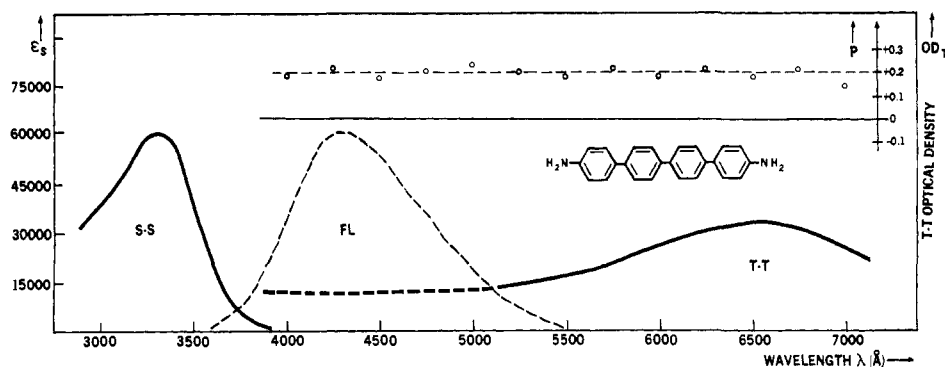
Figure 8. S–S and T–T absorption spectrum of p,p'-diaminoquaterphenyl in tetrahydro-2-methylfuran at 77°K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.
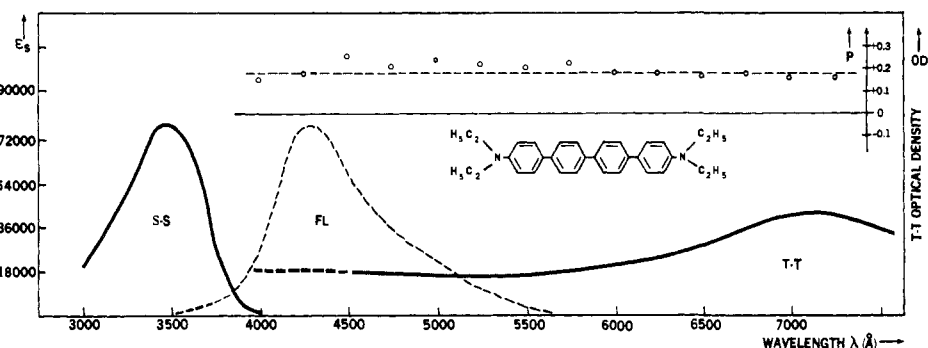

Figure 9. S–S and T–T absorption spectrum of p,p'-tetraethyldiaminoquaterphenyl in tetrahydro-2-methylfuran at 77°K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.
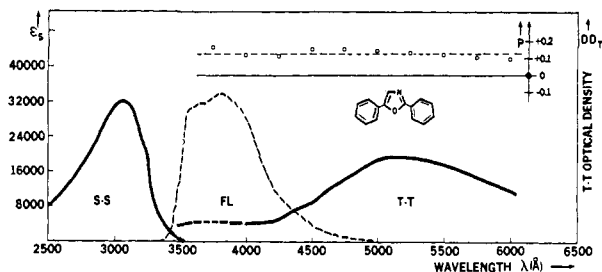

Figure 10. S–S and T–T absorption spectrum of 2,5-diphenyloxazole (PPO) in EPA at 77°K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.

Figure 11. S–S and T–T absorption spectrum of 2,5-di(4-biphenylyl)oxazole (BBO) in tetrahydro-2-methylfuran at 77°K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.
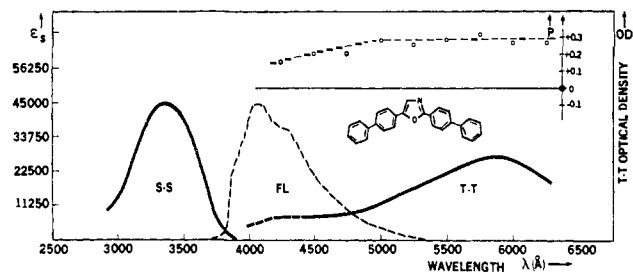
tion with regard to the strong T–T absorption band located at about 6000 Å. However, there is a change in the degree of polarization P in the fluorescence region in Figure 11. This would suggest the presence of another electronic transition. We cannot explain its origin. It seems to be real and not to have resulted from an impurity. This change in P was originally observed in a sample of BBO obtained from K & K Laboratories. The same compound was obtained from Sigma Chemical Co. The sample was zone refined many times. There was no noticeable change in the appearance of the T–T absorption or in the polarization curves of the two samples. Because the differently polarized T–T absorption band is positioned too far from the S–S absorption band, no attempt was made to obtain the substituted compound.

2,2'-p-Phenylenebis(5-phenyloxazole)   (POPOP).[25]

(25) H. W. Furumoto and H. L. Ceccon, *J. Appl. Phys.*, **40**, 4204 (1969).

According to Figure 12, the positive degree of polarization P of the broad T–T absorption band again indicates an A_2a constellation. For the same reasons applied to the absorption spectra of PPO, the S–S and the T–T absorption bands should be positioned along the long axis of the molecule.

Dibutoxy-POPOP. In Figure 13 we have presented the spectra of the long-axis-substituted POPOP. Although the S–S absorption maximum has red shifted only about 100 Å, the T–T absorption band seems to have shifted about 900 Å, leaving only its rather weak tail to overlap with the fluorescence region. This large red shift of the T–T absorption maximum is remarkable. The alkoxy group, which is only a mildly active auxochrome in the singlet manifold, seems to be a rather strong one in the triplet manifold. It seems that it almost equals the red shift obtained by the two amino groups in p-terphenyl, which was about 1000 Å. The
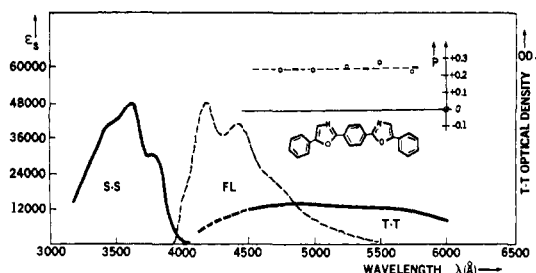
Figure 12. S–S and T–T absorption spectrum of 2,2'-p-phenylene-bis(5-phenyloxazole) (POPOP) in tetrahydro-2-methylfuran at 77°K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.

Figure 13. S–S and T–T absorption spectrum of 1,4-bis(5-p-n-butoxyphenyloxazole) (dibutoxy-POPOP) in tetrahydro-2-methyl-furan at 77°K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.

large red shift resulting from the butoxy substitution suggests the following. In many cases it might be of advantage to perform an alkoxy group substitution, instead of an amino group substitution, to red shift a T–T absorption band in an A_2a constellation.

It should also be noted that a long-axis substitution in POPOP caused the red shifts of the S–S and T–T absorption bands. This confirms our reasoning that both oscillators are indeed positioned along the long axis of the molecule.

The compound could be lased with ease on the AVCO nitrogen laser. Using a polar solvent such as dimethyl sulfoxide, emission occurred in the blue-green, although peak response was in the blue region. Acidifying a solution of the dye changed fluorescence from blue-green to orange, with minimal change of the absorption spectrum. Other POPOP dyes show this "exciplex" behavior, and on steadily acidifying the original solution, the fluorescence changed from the blue-green to white (the sum of the blue-green and the orange from 4000 to 6500 Å) to orange. The dye could not be made to lase in the orange region in acid solution, however.

2-(1-Naphthyl)-5-phenyloxazole (α-NPO).[6] The electronic spectra of this compound are presented in Figure 14. As expected, this molecule also has rather low T–T absorption over the fluorescence region. The ϕ_F = 0.94[2b] is rather high. However, the polarization curve indicates the presence of several overlapping transitions. We conclude that α-NPO does not exhibit a favorable constellation.[26]

Discussion

A. The Organic Scintillators. We summarize some of the more important experimental results and conclusions on the laser action and spectroscopic properties of these compounds.

1. As expected, there is rather little T–T absorption present over the fluorescence region of the organic scintillators investigated. According to Bensasson and Land,[27] for p-terphenyl at the maximum of the T–T absorption: $\epsilon_T(4600 \text{ Å}) = 9 \times 10^4$ l./(mol cm). From Figure 4, one can estimate the T–T absorption over the fluorescence region to be about $\epsilon_T(3400 \text{ Å}) \sim 4 \times 10^3$ l./(mol cm). Because the organic scintillators possess also rather high fluorescence quantum yields ϕ_F, their ability to exhibit laser action under flashlamp
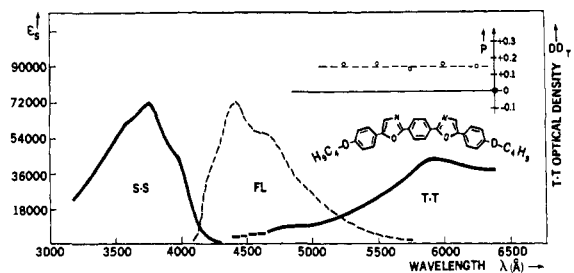
Figure 14. S–S and T–T absorption spectrum of 2-(1-naphthyl)-5-phenyloxazole (α-NPO) in 3-methylpentane at 77°K. The degree of polarization P is presented on top of the T–T absorption spectrum. The fluorescence spectrum FL is shown by a dashed curve.

excitation is easily understood. The ϕ_F's for p-terphenyl, p-quaterphenyl, and POPOP are 0.93, 0.89, and 0.93, respectively.[2b]

Nevertheless, if compounds were available with less T–T absorption over the fluorescence region and ϕ_F even closer to unity, more efficient laser action would result. Surprisingly, some methyl-substituted p-oligophenylenes, such as 3,3''-dimethyl-p-quaterphenyl,[2b] have a ϕ_F very close to unity. These compounds could have a lower laser action threshold compared to the unsubstituted compounds.

2. Unexpected and very important was the finding that most of the organic scintillators which belonged to the B(a) class had A_2a constellations. Most likely, some of the organic scintillators which show laser action under flashlamp excitation, and which we have not studied, could show similar promising properties.[28] In addition, there are many organic scintillators which do not show laser action under flashlamp excitation. There is also a very large reservoir of chain-type molecules available belonging to the B(a) class and not classified as organic scintillators. Many of them show more or less strong fluorescence. They may consist of oxazole, oxadiazol, furan rings connected to phenyl rings, polyenes with phenyl rings at both ends, or indole substituted by phenyl group(s).[2b] Combinations containing acetylenes or of indole or polyenes connected to five-membered heterocyclics should also be investigated.

B. The Substituted Organic Scintillators. Also here we have some expected and some unexpected results. (1) As expected, the introduction of auxochromic groups in the para positions has produced

(26) Most likely, the appearance of T–T absorption bands with mixed polarization can also be expected for the other B(b) type of molecules.

(27) R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, **67**, 1904 (1971).
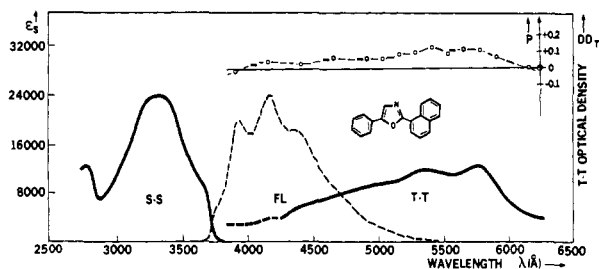
(28) ϕ_F in the oligophenylenes (and their derivatives) should be increased by fixing the rings coplanar to each other by CH bridges, e.g., switching from biphenyl to fluorene or 9,10-dihydrophenanthrene, from p-terphenyl to 2,2'-methylene-5',6''-methylene-p-terphenyl.

rather large red shifts of the T–T absorption spectra. Significantly, the introduction of the butoxy groups has resulted in a red shift of the T–T absorption spectra which is almost as large as the one resulting from the diamino groups. Because the butoxy groups seem not to "smear out" the T–T absorption spectrum, the butoxy group might be superior to the amino group. In addition, this group does not introduce the weak C–N single bond. (2) Rather unexpected and undesired is the flatness of the T–T absorption bands in the amino-substituted polyphenyls. The broadening of the T–T absorption bands negates to a very large extent the large red shifts of these bands. The obvious reason for the broad T–T absorption bands is that the molecule in its triplet state is not coplanar.

If, upon excitation, the molecular geometry changes, the absorption bands are expected to be broad, due to the large Franck–Condon factors. In these terphenyl type molecules, the degree of planarity is expected to be sensitive to type of electronic excited state and can thus account for the observed broad T–T absorption bands.

Noncoplanarity has an effect not only on $\epsilon_T(\lambda_F)$ but also on quantum efficiency ϕ_F. It reduces ϕ_T, increasing n_{T_1}.

It is well known that when the amino group and, to some extent, the other auxochromic groups are not coplanar with the aromatic ring(s), the rates for the transitions $T_1 \rightarrow S_0$ (phosphorescence) and $S_1 \rightarrow T_1$ (intersystem crossing) are considerably larger than those of the unsubstituted compounds.[29–31]

One can counter the broadening of the T–T absorption bands and also increase quantum efficiency ϕ_F (reducing n_{T_1}), thereby improving the efficiency of organic laser dye materials, by chemical modification; e.g., for an auxochromic group such as the amino, one can restrict the system to coplanarity in cyclic structures.
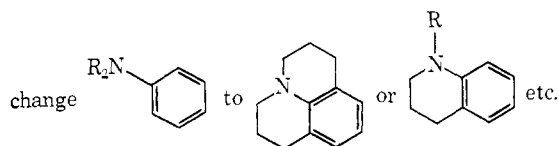
This should diminish nonradiative deactivation of the excited state by reducing internal mobility of the organic dye[32] and at the same time should tie down the single C–N bond, often the weakest bond in such a molecule, to improve stability.

Spectroscopic data may be useful in comparing laser dyes. A_2a (organic scintillator laser dyes) and A_2c type laser dyes could be crudely characterized by wavelength distance (in ångströms) between the fluorescence maximum and the maximum of the T–T absorption band positioned to longer wavelengths. The farther away from the fluorescence region the T–T absorption band is located, the less the T–T absorption will be.

In Table I we compare 7-diethylamino-4-methylcoumarin with the compounds we studied. With respect to T–T absorption it is apparent from the table that

Table I. Location of the Fluorescence Maximum (FL), T–T Absorption Maximum (T–T), Together with the Separation ($\Delta\lambda$) between the Two Maxima of 7-Diethylamino-4-methylcoumarin and the Compounds Studied in This Work

Compd	FL, Å	T–T, Å	$\Delta\lambda$, Å
7-Diethylamino-4-methylcoumarin	4300	6000	1700
p-Terphenyl	3400	4600	1200
p,p'-Diaminoterphenyl	4000	5600	1600
p,p'-Diethylaminoterphenyl	4150	6100	1950
p-Quaterphenyl	3700	5300	1600
p,p'-Diaminoquaterphenyl	4300	6500	2200
p,p'-Diethylaminoquaterphenyl	4300	7100	2800
PPO	3800	5150	1350
BBO	4100	5900	1800
POPOP	4200	~5000	~800
p,p'-Dibutoxy-POPOP	4450	5900	1450
α-NPO	4000	5800	1800

the amino and diethylaminopolyphenyls hold the promise of being more efficient laser dyes than the 7-diethylamino-4-methylcoumarin (however, most of the spectral shifts of S–S, fluorescence, and T–T are fairly similar if expressed in terms of frequency instead of wavelength), provided, of course, that one forces the amino groups to be coplanar with the phenyl rings. As already mentioned, substitution of p-terphenyl and p-quaterphenyl at the p,p' positions by butoxy groups could also have improved their performance.[33]

General Considerations

An intriguing question arises. One may ask, which chromophore (parent aromatic compound) after substitution would give the laser dye with the lowest laser action threshold and the highest efficiency? Or to put the question differently; has the most efficient laser dye yet been synthesized? Without question, one would have to start with a chromophore which has a $B_1a(C_1a)$ constellation. Next best would be the subcase to the $A_2a(D_2a)$ case.

Using data from literature and data obtained at this laboratory on the S–S and T–T absorption bands of some aromatic compounds and their polarizations, we will try to classify some commercially available prototypes of organic dye laser materials which show laser action when flashlamp pumped. This discussion is important in two ways. First, it will clarify why some other molecules we have not discussed here show laser action and why so very many other organic dyes show no laser action at all. Second, and more significant, it will indicate which classes of chromophores are promising candidates for new laser materials after substitution.

2-Hydroxy-4-methyl-7-aminoquinoline.[34] The spectroscopic properties of quinoline are similar to those of naphthalene (i.e., T–T and S–S absorption). Naphthalene has been studied extensively. We summarize briefly some of the most important data, since they are important for the understanding of the laser action properties of several laser dyes. The fluorescence quantum

(29) E. C. Lim and S. K. Chakrabarti, Chem. Phys. Lett., 1, 28 (1967); J. Chem. Phys., 47, 4726 (1967).
(30) M. Kasha and H. R. Rawls, Photochem. Photobiol., 7, 561 (1968).
(31) E. C. Lim and M. Kedzierski, Chem. Phys. Lett., 20, 242 (1973).
(32) K. H. Drexhage, "Laser Focus," March, New York, N.Y., 1973, p 35.

(33) It is interesting to note that the ϕ_F's of p,p'-dihexahydrofarnesoxy-p-terphenyl (0.97) and p,p'-dibutyloctoxy-p-quaterphenyl (0.93) are higher than those of p-terphenyl (0.93) and p-quaterphenyl (0.89), respectively.[2b]
(34) R. Srinivasan, IEEE J. Quantum Electron., 5, 552 (1969). This compound undoubtedly exists as the most stable paupomer, 7-amino-4-methyl-2-quinolone.

yield of naphthalene is $\phi_F = 0.23$.[2b] This molecule shows a weak S–S absorption band at about 3145 Å, followed by a strong one at about 2860 Å.
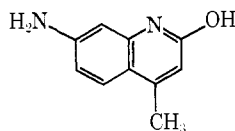

Platt[35] applied the free electron model successfully to naphthalene (and other catacondensed molecules) to correlate the energy values of its singlet levels with those of the other catacondensed aromatic compounds. For the first weak absorption band (the $^1L_b \rightarrow {}^1A$ transition in Platt's notation) at 3145 Å, the corresponding absorbing oscillator is positioned along the long axis of the molecule. The strong second absorption band ($^1L_a \rightarrow {}^1A$) at 2860 Å is short-axis polarized. Experimentally, due to vibronic–electronic mixing with the strong short-axis-polarized ^1L_a band, the first ^1L_b band in naphthalene is also mostly short-axis polarized.[36]

The T–T absorption spectrum of this molecule shows a strong transition in the blue-violet portion of the spectrum (the $^3B_{3g}{}^- \leftarrow {}^3B_{2u}{}^+$ transition), consisting of three strong and several weak lines. This band is polarized along the long axis of the molecule.[12] Therefore, naphthalene and most likely most of its heterocyclic derivatives (i.e., quinoline, coumarin) present an A_2a case. In 2-hydroxy-4-methyl-7-aminoquinoline we have an A_2c case. To the red side of this strong T–T absorption band of naphthalene, a very weak T–T absorption band stretches from about 4300 to 6000 Å. It consists of several lines showing mixed polarization. This indicates the presence of two electronic transitions in this region. One corresponds to an allowed, short-axis-polarized transition ($^3A_{1g}{}^- \leftarrow {}^3B_{2u}{}^+$). The second results from a forbidden transition.[37]

It is interesting to note that 2-hydroxy-4-methyl-7-aminoquinoline contains two auxochromic groups opposite to each other. The result would be a strong amplification and red shift of the long-axis-polarized low-energy S–S absorption band (corresponding to the $^1L_b \rightarrow {}^1A$ transition in naphthalene) and a strong intensification and, most likely, a very large red shift of the strong, long-axis-polarized T–T absorption band.

7-Diethylamino-4-methylcoumarin.[38] The spectroscopic properties of coumarin also resemble those of naphthalene. Coumarin exhibits two long-axis-polarized S–S absorption bands at 3250 and 2900 Å. A strong, short-axis-polarized band is located at 2250 Å. A strong, long-axis-polarized T–T absorption band has its maximum at about 4600 Å. Therefore, coumarin presents an A_2a situation.[3] Long-axis substitution (i.e., in the seven position) by an auxochromic group shifts the low-energy S–S absorption band (and also the fluorescence spectrum) to longer wavelengths. The long-axis-polarized T–T absorption band, however, undergoes an exceptionally large red shift of about 1300 Å. The fluorescence spectrum now falls on the rather weak tail of this band. Since many of the seven-substituted coumarin derivatives also fluoresce strongly,

these compounds show laser action under flashlamp excitation.[2a] The molar triplet extinction coefficient
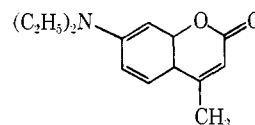
ϵ_T of 7-hydroxy-4-methylcoumarin at its maximum at about 5000 Å is about the same as ϵ_S at its maximum at 3250 Å.[3] Assuming the same is true for 7-diethylamino-4-methylcoumarin, one would have over the fluorescence region at about 4400 Å $\epsilon_T(\lambda_F) \sim 2 \times 10^3$ l./(mol cm).

9-Aminoacridine.[39] This molecule has been classified as a C_1b case.[3] It seems it is not an ideal C_1b case, since its fluorescence maximum at about 4600 Å should overlap with rather strong T–T absorption. In acridine, we have $\epsilon_T(4600 \text{ Å}) \sim 3 \times 10^3$ l./(mol cm).[40]

Brilliant Sulfaflavine.[39] This complicated compound could be viewed as a short-axis-substituted naphthalene molecule.

The strong short-axis interaction resonance substitution has the effect that the strong second absorption band in naphthalene ($^1L_a \leftarrow {}^1A$) which was short-axis
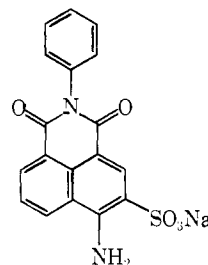
polarized experiences an exceptionally large red shift. Its energy might have become lower than that of both the weak, long-axis-polarized S–S absorption band ($^1L_b \leftarrow {}^1A$) and the strong, long-axis-polarized T–T absorption band in the blue region. So far, we have an ideal C_1b case (corresponding to B_1c). As mentioned, naphthalene (and probably most of its heterocyclic derivatives) has a weak T–T absorption band located to the long-wavelength side of the strong T–T transition, covering the region from about 4300 to 6000 Å. Besides a forbidden transition, there is also a short-axis-polarized allowed transition ($^3A_{1g}{}^- \leftarrow {}^3B_{2u}{}^+$).[37] This latter transition would also have been intensified by the short-axis substitution. As a result, rather strong T–T absorption is present over the fluorescence region of brilliant sulfaflavine.

Therefore, we do not have the ideal case C_1b, although this molecule has a rather low laser action threshold.[39] This may be the result of a fluorescence quantum yield ϕ_F close to unity.

At the fluorescence maximum at 5200 Å of brilliant sulfaflavine, $\epsilon_T(\lambda_F) \sim 1.6 \times 10^3$ l./(mol cm).[9]

Rhodamine 6G.[38] Discussion of the laser action properties of this compound also covers the other xanthene dyes (fluorescein, rhodamine B, etc.). From the structure of rhodamine 6G it is apparent that we have strong resonance across the molecule. Un-

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(40) A. Kellmann and L. Lindqvist, "The Triplet State," A. B. Zahlan, Ed., Cambridge Press, Cambridge, England, 1967, p 439.
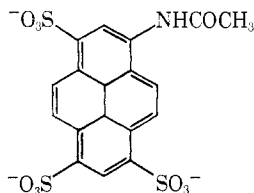
fortunately, no polarization data or even T–T absorption data are available on xanthene. In a very rough approximation, the xanthene molecule may be viewed as having spectroscopic properties similar to those of anthracene. There, the strong $S_0 \rightarrow S_1$ ($^1L_a \leftarrow {}^1A$) transition is short-axis polarized. It covers the long-axis polarized $^1L_b \leftarrow {}^1A$ transition. A strong, long-axis
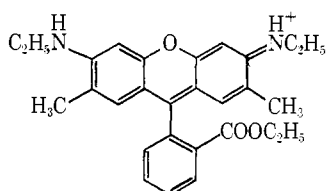
polarized T–T absorption band is located in the blue region.[22] This suggests a subcase to an A_2a constellation. Strong resonance across the long molecular axis due to the long-axis substitution would very much amplify and red shift the original weak, long-axis-polarized $^1L_b \leftarrow {}^1A$ transition. The strong, long-axis-polarized T–T absorption band, however, would have been even more red shifted than the long-axis-polarized $^1L_b \leftarrow {}^1A$ absorption band as a result of the introduction of the two $N(C_2H_5)_2$ groups. Rhodamine 6G most likely presents a subcase to A_2c.

The T–T absorption spectrum and the molar triplet extinction coefficient of rhodamine 6G have been measured by Buettner, et al.[41] The spectrum shows a weak band with its maximum located at about 6200 Å. It is doubtful that this band corresponds to the original one, probably located in the blue region in xanthene. In xanthene, the lowest energy S–S absorption band is located at about 2900 Å[42] and in rhodamine 6G[2b] at 5300 Å. If one assumes that the T–T absorption has been red shifted at least twice that amount, it must be positioned in the 9000-Å region.[43] The weak T–T absorption band located at 6200 Å could be a vibrational progression of the strong one. According to ref 41 $\epsilon_T(\lambda_F) \sim 1.3 \times 10^3$ l./(mol cm) in the fluorescence region of rhodamine 6G.

3-Monoacetylaminopyrene-5,8,10-trisulfonate.[44] It is not possible to classify this laser dye, since the amino group forms an angle between the short and long axes of the molecule. The strong T–T absorption band ($^3A_g{}^- \leftarrow {}^3B_{2u}{}^+$) at about 4100 Å is long-axis and the

weaker one ($^3B_{3g}{}^- \leftarrow {}^3B_{2u}{}^+$) at about 5300 Å is short-axis polarized.[45,46] Substitution at about 45° should red shift and intensify both bands. There should be rather strong T–T absorption over the fluorescence region (green). The fluorescence maximum should fall on the rather strong tail of the red shifted band, which corresponds to the $^3B_{3g}{}^- \leftarrow {}^3B_{2u}{}^+$ transition in pyrene.

Conclusions

1. From the experimental data available on molar triplet extinction coefficients $\epsilon_T(\lambda_F)$ over the fluorescence region of laser dyes, it seems that rhodamine 6G with $\epsilon_T(\lambda_F) \sim 1.3 \times 10^3$ l./(mol cm) has probably the lowest laser action threshold of all commercially available organic laser dyes. For most other laser dyes, probably $\epsilon_T(\lambda_F) \sim 1$–5 $\times 10^3$ l./(mol cm). The reasons for this rather high value of $\epsilon_T(\lambda_F)$ are the following. Most of the commercially available laser dyes which show laser action under flashlamp excitation belong to the A_2c group. Surprisingly, it seems that an ideal $B_1c(C_1b)$ constellation has not yet been synthesized. In brilliant sulfaflavin and 9-aminoacridine a closely positioned T–T absorption band has-been overtaken by a differently polarized S–S absorption band. However, to the long-wavelength side of the strong T–T absorption bands located in the blue spectral region of naphthalene and anthracene (and their heterocyclic derivatives) there is still a broad region of considerable T–T absorption present, which now overlaps with the fluorescence (laser action) region. There is no reason why, with the suggestions and spectroscopic equipment used in this article, it should not be possible to monitor the synthesis of new laser dyes which have only $\epsilon_T(\lambda_F) \sim 1$–5 $\times 10^2$ l./(mol cm). With the exception of PPO, there is no laser dye which has a better ϕ_F than 0.93.[2b] Obviously, it should also be possible to synthesize laser dyes which have a ϕ_F of 0.98 or better.[47] These new compounds (super laser dyes) should have a much lower laser action threshold and a much higher efficiency than any others currently on the market.

2. One may ask next, which chromophores possess an ideal $B_1a(C_1a)$ constellation? Unfortunately, due to the scarcity of polarization data on T–T absorption bands,[22] we are unable to suggest many candidates. Tetracene seems to present a possibility.[8] Short-axis substitution by one or two alkoxy groups[48] could shift the lowest energy S–S absorption, where no T–T absorption is detectable. The main prerequisite for the substituted compound to show laser action would be a high ϕ_F.

Significantly, BBO showed a negatively polarized T–T absorption band in its fluorescence region. The energy gap between this band and the lowest energy S–S absorption band seems to be too large to be bridged by a red shift of this S–S absorption band following substitution. However, there exists the possibility that among compounds similar in structure to BBO there might be some exhibiting a more promising B_1a situation.

Lacking a large reservoir of chromophores with

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(42) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, N. Y., 1951, No. 133.

(43) It is experimentally rather simple to determine whether a laser dye has resulted from a chromophore with A_2a type of constellation. One excites into the lowest energy S–S absorption band. In an A_2c constellation, there always must be a T–T band positioned to the red side of the fluorescence spectrum, exhibiting positive polarization. To verify the presence of an A_2c constellation in rhodamine 6G, using the experimental setup employed in this study, one could very efficiently excite the compound with the 5145-Å line from a continuous wave ion argon laser.

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(46) J. Langelaar, J. Wegdam-Van Beck, H. Ten Brink, and J. D. W. Van Voorst, Chem. Phys. Lett., 6, 460 (1970).

(47) In ref 6, a table of quantum fluorescence yields of some laser dyes is presented. Rhodamine 6G: ϕ_F = 0.84 only.

(48) Substituted tetracene should be chemically and photochemically rather unstable.

$B_1a(C_1a)$ constellations, one has to reconsider the A_2a types. The larger the energy gap between the lowest energy S–S and the T–T absorption bands in this type of chromophore the lower the T–T absorption over the fluorescence region of the substituted compound (the A_2c type of laser dye) will be. All the A_2c type of commercially available laser dyes we discussed had either naphthalene or anthracene (or their heterocyclic derivatives such as coumarin and xanthene) as chromophores. In both compounds, the energy gap between the lowest energy S–S and T–T absorption bands is not very large. As a result of this situation, after substitution, the spectral region of laser action still falls on a region of considerable T–T absorption. However, improvements in laser dye performance can be expected if one starts with chromophores which have a larger energy gap. We have not emphasized the reduction of intersystem crossing rates, but certainly T–T absorption can be minimized by this approach.

Obviously, the final conclusion of this paper has already been made. At the moment, the chain-type compounds present a very large pool of promising molecules. Among them, there should be many candidates possessing promising A_2a constellations.

Gas Phase Fluorination of Benzene, Fluorobenzene, m-Difluorobenzene, and Trifluoromethylbenzene by Reactions of Thermal Fluorine-18 Atoms[1]

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Abstract: Thermal fluorine-18 atoms have been reacted in the gas phase with benzene, fluorobenzene, m-difluorobenzene, and trifluoromethylbenzene. The ^{18}F atoms were formed at high kinetic energies by the $^{19}F(n,2n)^{18}F$ nuclear reaction and then thermalized by multiple collisions with SF_6. The yields of $^{18}F/H$ are small and pressure independent in the absence of oxygen. With O_2 present, the yields increase substantially, reaching >60% for $C_6H_5{}^{18}F$ from C_6H_6. The yield from substitution of thermal ^{18}F for H ortho to another F substituent is decreased by O_2, while that in meta and para positions is substantially increased. No such diminution of yield in the ortho position is found for CF_3 as a substituent. The substitution of thermal ^{18}F for aromatically bonded F atoms is observed in low yields only.

Relatively few experimental investigations have been carried out which unambiguously involve the reactions of atomic fluorine with aromatic systems despite the considerable interest in such reactions.[2] However, radioactive ^{18}F atoms ($t_{1/2} = 110$ min) can be produced by various nuclear reactions, including the $^{19}F(n,2n)^{18}F$ reaction with fast neutrons, and these atoms can be brought to thermal energies without bond formation by multiple collisions with suitable inert moderators.[3-13]

In the last several years, research in this laboratory has utilized such thermal ^{18}F atoms for reaction studies with olefins,[6,7,9,10] acetylene,[8] various RH compounds,[11] and a variety of inorganic species.[12,13]

Several earlier studies have been made of ^{18}F atomic reactions in aromatic systems, but these have generally involved either a neat fluoroaromatic substrate or else a relatively high concentration of aromatic substrate, such that the observed reaction products are formed by a mixture of kinetically hot and thermal processes.[14-23] In those experiments, none of the high moderation systems were studied in which the observed products are essentially those of thermal origin. Condensed phase experiments have involved ^{18}F atoms from either the (n,2n) or (γ,n) reactions on fluorinated sub-

(1) This research was supported by A.E.C. Contract No. (04-3)-34, Agreement No. 126.

(2) Many experiments result in fluorination of aromatic compounds but under conditions in which both atomic and molecular fluorination mechanisms can be readily postulated. See, for example, V. Grakauskas, *J. Org. Chem.*, 35, 723 (1970); V. Grakauskas, *Intra-Sci. Chem. Rep.*, 5, 85 (1971).

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