

DYESTUFF LASERS AND LIGHT COLLECTORS - TWO NEW FIELDS OF APPLICATION FOR FLUORESCENT HETEROCYCLIC COMPOUNDS

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Abstract — The physical principles and methods of the functioning of fluorescent solar collectors and dyestuff lasers are briefly discussed, together with the demands that have to be met by a fluorescent dyestuff.

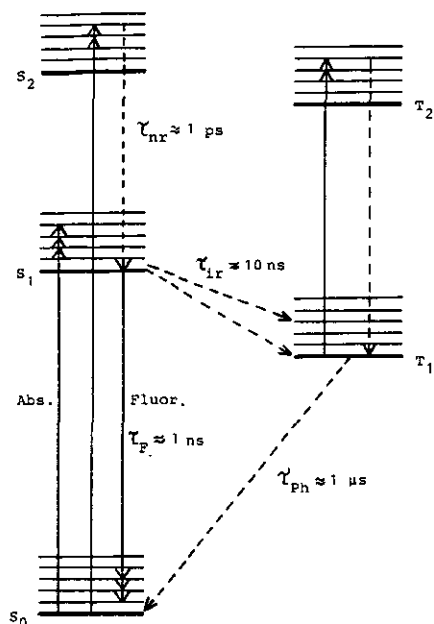
In a summary of recent work carried out in these two fields, a report is given of perylene carboxylic ester dyes and perylene tetracarboxylic acid diimide dyes for solar collectors, bifluorophoric laser dyes, laser dyes with intramolecular triplet quenching and infrared laser dyes with pyrylium and thiapyrylium terminal systems, also from the tetra and hexamethine hemicyanine ranges.

A study was made of the effect of cyanogen substitution on the fluorescence quantum yield in coumarin and xanthene dyestuffs. Among the coumarin dyestuffs are compounds suitable as energy converters in light collecting systems, particularly if the amino group is fixed by ring closure to the aromatic system as high-power laser dyestuffs.

In recent years, two promising new fields of application have been developed for fluorescent dyestuffs: 1) as an active medium in dye lasers and 2) in light collectors and solar collectors.

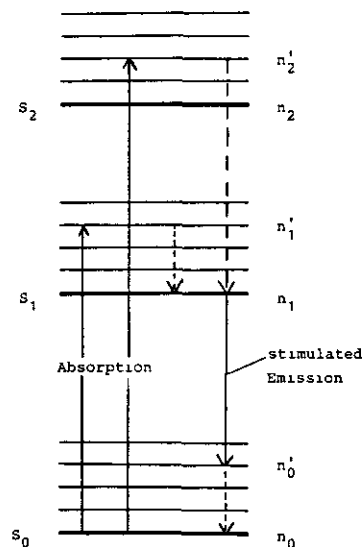
The laser is an optical device for the amplification of radiation, by definition: Light Amplification by Stimulated Emission of Radiation. Gases and solids can serve as the active medium; with the dye laser¹, the active medium is a solution of a

fluorescent dyestuff.



Eigenstates of a typical dye molecule with radiative (solid lines) and non-radiative (broken lines) transitions

Fig. 1



Pump cycle of dye molecules

Fig. 2

By the absorption of light, dyestuff molecules are transformed from the ground level S_0 into the excited level S_1 . The energy absorbed as a result can either be emitted directly in the form of light (fluorescence) or by spin flip, when the much longer-lasting triplet state is reached (phosphorescence). A third possibility is non-radiative disactivation. Here the dyestuff releases its energy as rotational or vibrational energy (fig. 1). If a high population density in the excited S_1 level now is reached by very intensive irradiation, an emitted light quantum can cause other molecules to release energy. By this reaction, further quanta with equal phase are obtained. These quanta themselves cause the light amplification. This population inversion is achieved in the case of the dyestuff laser in the following manner (fig. 2):

During absorption the dyestuff molecule shifts into higher vibrational states of the S_1 level. The vibrational energy is given off within a few pico-seconds non-radiatively to the liquid, and the S_1 ground state is reached. The light quanta absorbed under continual radiation, thus repeatedly come across the emptied vibrational level of S_1 , since the fluorescent life of the S_1 ground state is in the

nanoseconds range, one thousand times higher than that of the higher vibrational states. Fluorescence leads in turn to higher vibrational levels of the S_0 state, which also rapidly becomes empty by non-radiative disactivation. The stimulated emission thus takes place with a transition from the S_1 ground state into the vibrational level of the S_0 state. The population inversion is reached, since the probability of presence in the S_1 ground state lies in the nanoseconds range, whereas in the vibrational level of the S_0 state, it amounts only to pico-seconds.

The dyestuff laser has met with particular interest because of its tunability. While gas and solid-state lasers can emit laser light of single wavelengths only, it is possible within the fluorescence band of a dyestuff (between 10 and 100 nm) to produce laser light of any wavelength in narrowband form by means of a suitable test set-up. The wide fluorescence band of the dyestuff compared with atomic spectra is understandable, if we consider that a typical dyestuff molecule contains 50 or more atoms, which are able to carry out a large number of vibrations against each other. These transitions into the various vibrational levels cause a dense line spectrum, which presents itself in the form of the fluorescence band (fig. 3).

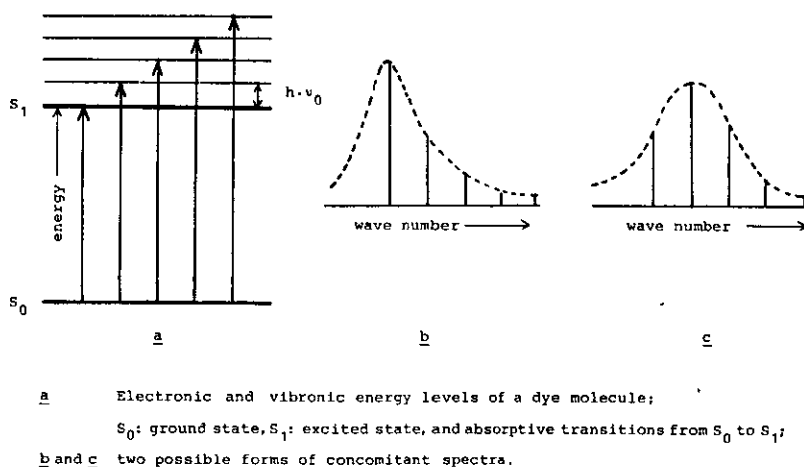
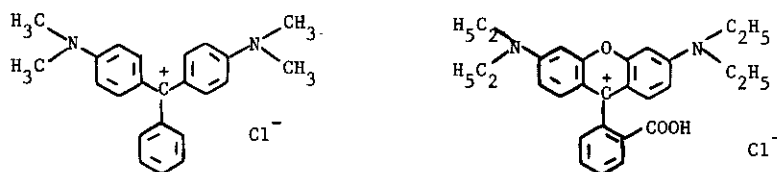


Fig. 3

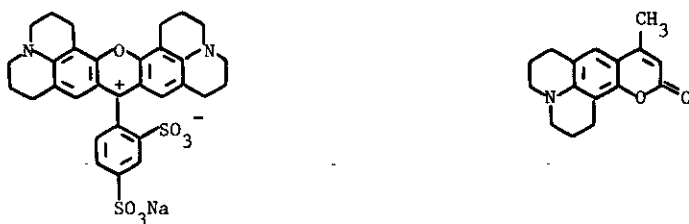
The excitation of the dyestuff molecules, also called optical pumping, can be carried out by flash-lamp or laser light. If the irradiated impulses are very short, then the dyestuff laser light will also be emitted in single pulses. The opposite is the continuous-wave laser, which supplies an uninterrupted emission of laser light. The nitrogen laser and the noble gas excimer laser are suitable for exciting the dyestuff molecules by pulses; the argon and krypton ion laser can be used

as a source of excitation for continuous wave operation.

A laser dyestuff must therefore have a high fluorescence quantum yield. In other words, it should not lose its absorbed light energy by non-radiative disactivation or by transition into the triplet state. The fluorescence quantum yield can be increased by restricting the opportunities for non-radiative disactivation. It can be done, for example, by means of a ring closure. Whereas malachite green has virtually no fluorescence, highly fluorescent xanthenes can be obtained by ring closure with oxygen.

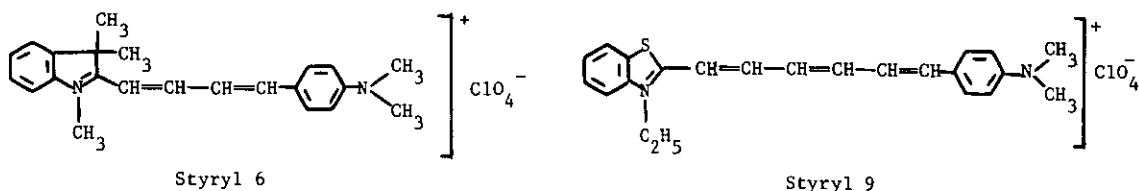


The oxygen ring closure hinders the phenyl nuclei from rotating. However, an energy loss also occurs on rotation of the amino groups. Drexhage was able to show this with the example of rhodamine B². The fluorescence quantum yield of this dyestuff is approx. 40 % at room temperature and can be increased to nearly 100 % by lowering the temperature, whereas it is only a few percent at the boiling point of ethanol. If we now link both alkyl radicals with the aromatic ring, the mobility of the amino groups is decreased considerably. In this way Drexhage obtained the rigidized laser dyestuffs with increased fluorescence quantum yield.^{2,3}



Before I proceed to our own work, I would like to mention a few of the important studies carried out during the last few years in the field of laser dyes. With polymethine dyestuffs, the rule applies generally, and with a high degree of accuracy, that extending the methine chain by one vinyl group brings about a bathochromic shift in the absorption maximum of 127 nm. Laser dyestuffs for the infra-red spectral range must therefore have a methine chain of at least four members.

Kato synthesized dyestuffs of the hemicyanine class with high stability and laser efficiency⁴. Examples are styryl 6 and styryl 9:



The broad tuning range and high laser efficiency are evident from the following diagram (fig. 4):

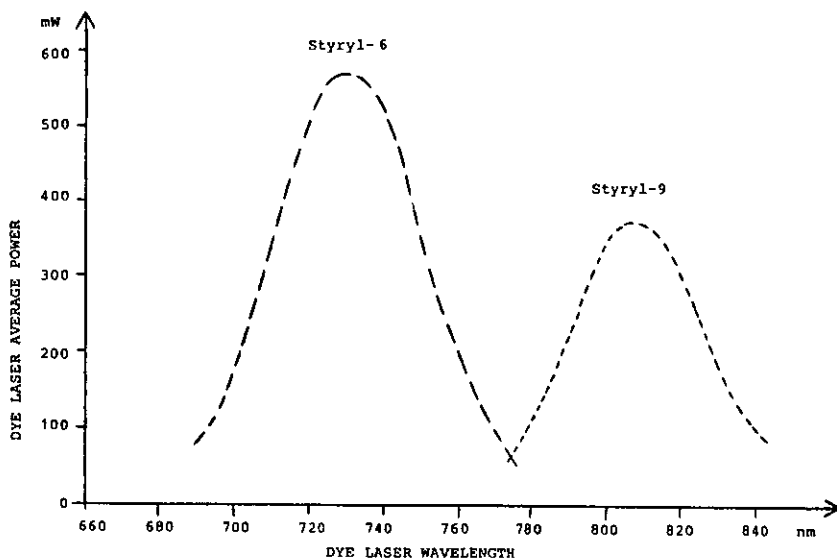
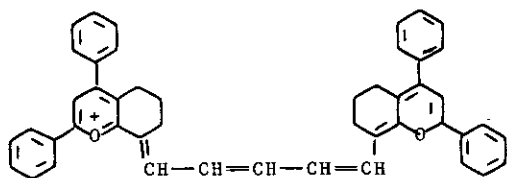


Fig. 4

A neodymium YAG laser (neodymium-doped Yttrium Aluminium Garnet) was used for stimulation.

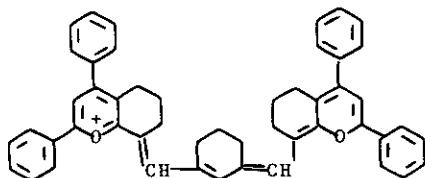
The pyrylium and the thiapyrylium ring are particularly suitable as terminal heterocycles for infrared-absorbing dyestuffs. Both shift the absorption well into the long-wave range, compared with other heterocycles. The disadvantage of these dyestuffs is their low stability. Drexhage was able to show that, by incorporating the polymethine chain in ring systems, it was possible to increase the photochemical stability several times⁵.

Stability of heptamethine cyanines

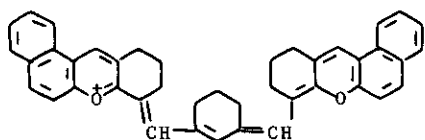


Photochemical stability

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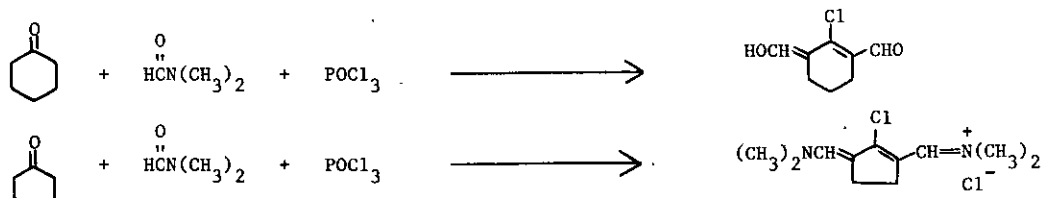
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According to the electron gas model for the π -electron system of the cyanine dye-stuffs, it was to be expected that substitution of the hydrogen on the central carbon atom of the heptamethine dyestuffs by a more strongly electronegative atom would cause a further shift of the absorption band into the long-wave range.

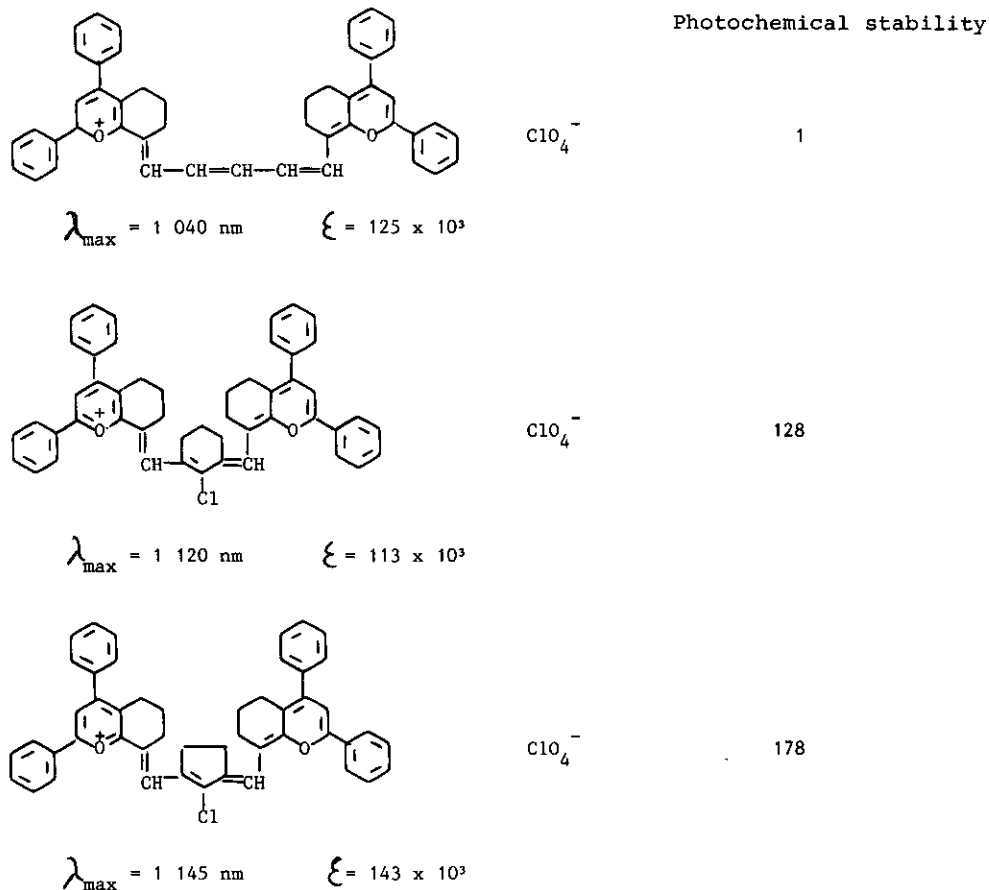
Zemlicka and Arnold⁶ obtained a suitable intermediate for producing dyestuffs of this kind by reacting cyclohexanone with phosphorus oxychloride and dimethylformamide according to Vilsmeier. From cyclopentanone, we can obtain the enamine, which is also suitable as an intermediate product.



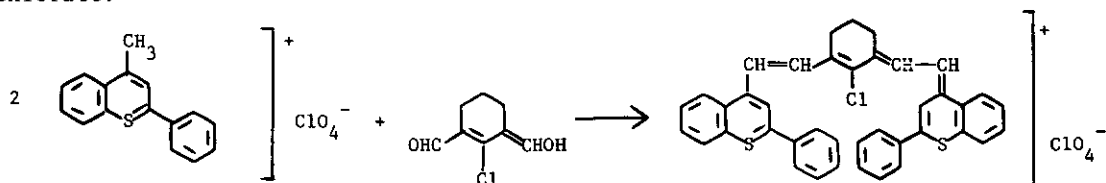
Reacting these bifunctional intermediates with 2,4-diphenyl-5,6,7,8-tetrahydro-1-benzopyrylium perchlorate results in highly stable laser dyestuffs for the infra-red range⁷. If we put the stability of the dye with a methine chain of five carbon atoms equal to 1, the relative stability will be 128 for the dyestuff in which three

carbon atoms are bound in a six-membered ring, and 178 for the dyestuff in which the three carbon atoms are built into a five-membered ring. The absorption maximum of the six-membered ring dyestuff with hydrogen instead of chlorine is 1090 nm. As a result of the chlorine substitution the bathochromic shift amounts to 30 nm. Going from the six-membered to the five-membered ring, we find a further bathochromic shift of 25 nm.

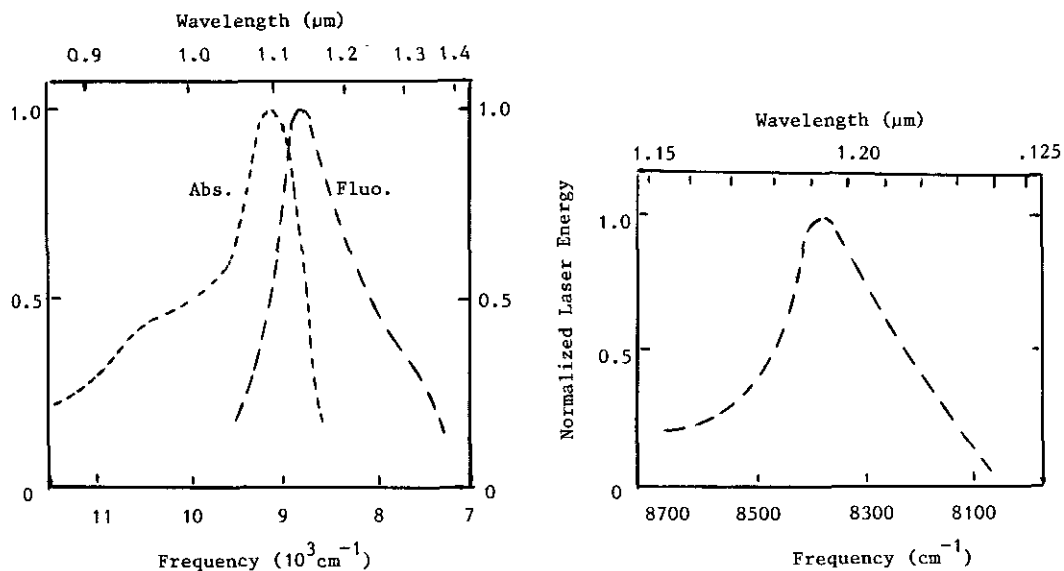
Stability of heptamethine cyanines



A particularly stable infrared laser dye can be obtained by reacting the Vilsmeier reaction product of cyclohexanone with 2-phenyl-4-methyl-5,6-benzothiazopyrylium perchlorate.⁸



The following diagram (fig. 5) shows the fluorescence and absorption curve as well as the broad tuning range of this dye.



Absorption and fluorescence spectra in 1,2-dichloroethane.

Tuning range. The dye laser is synchronously pumped by a YAG-laser.

Fig. 5

One disadvantage of the dye laser, and one which limits its use in the preparative sector, is its low energy efficiency. Although energy efficiencies of 50 % are reached with the laser-pumped dye laser, this level of conversion of pumping light into dye laser emission must also be multiplied by the efficiency of the pump laser. Since the latter is always less than 0.5 %, it is also the upper limit of the total energy efficiency of a laser-pumped dye laser. With flash lamp-pumped dye lasers, efficiencies of 0.8 % are achieved with the most effective laser dyestuffs, such as rhodamine 6G. This is understandable if we see what a small proportion of the flash lamp light rhodamine 6G is able to absorb (fig. 6).⁹

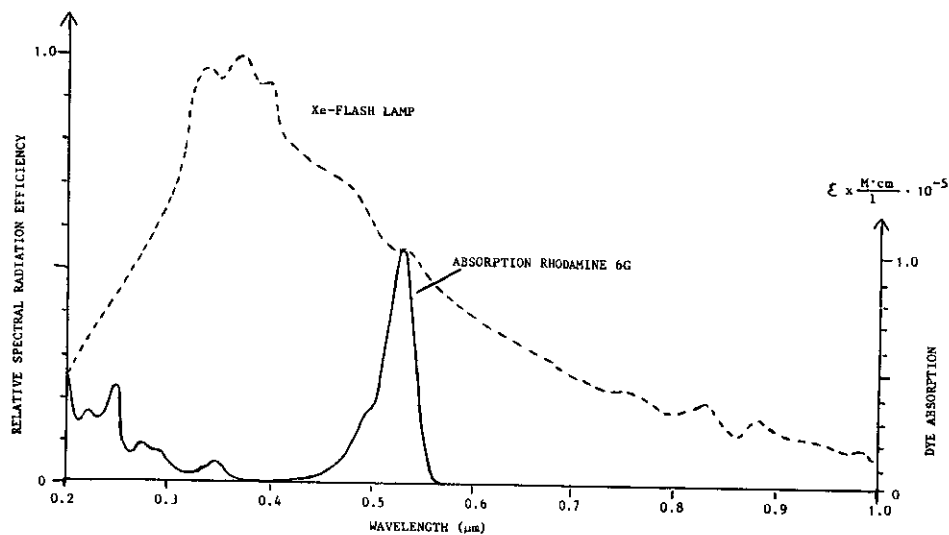


Fig. 6

The useful percentage of the flash light ought to be higher if the solution contains a second fluorescent dyestuff whose fluorescence is at the absorption wavelength of the first laser dye. Should the transfer of energy be non-radiative, the distance of molecules between the two dyestuffs must be very small indeed. It is from this that Lüttke and Schäfer derived the idea of bifluorophorous dyestuffs.¹⁰ They found a suitable system in the combination of terphenyl and POPOP, named from the alternating linkage of phenyl and oxazole radicals. The joint graph of the absorption and fluorescence spectra of both compounds (fig. 7) shows how favourably the fluorescence spectrum of *p*-terphenyl lies in the absorption spectrum of POPOP.

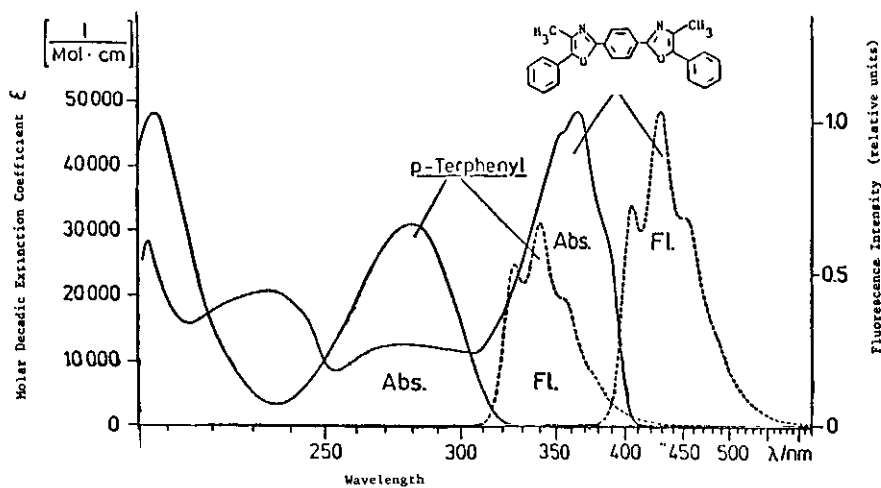


Fig. 7

If we link both compounds via a methylene bridge, only the fluorescence of POPOP remains; the excitation energy of the terphenyl has thus been transferred completely and non-radiatively to the acceptor dyestuff (fig. 8).

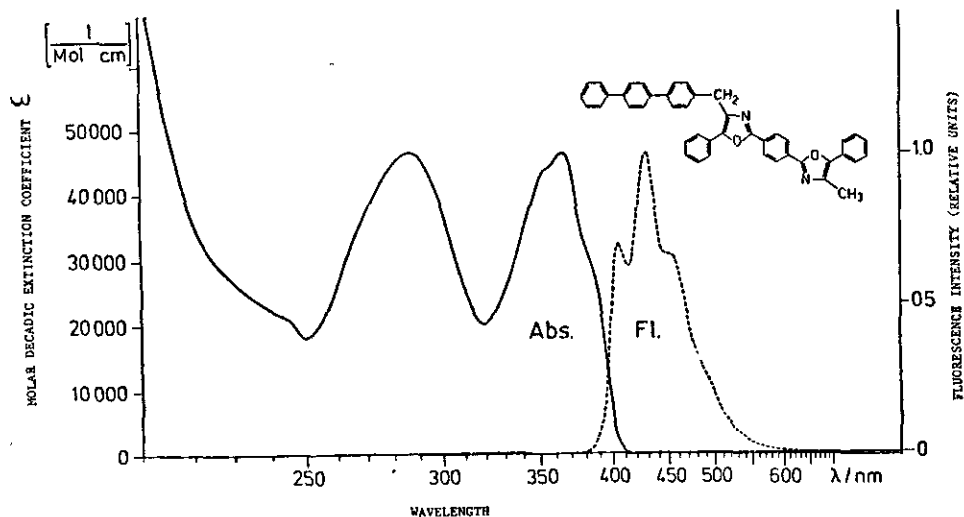


Fig. 8

The peak output energy of the new dyestuff is about 30 % higher than that of the oxazole dyestuff, corresponding to the higher absorption in the new molecule brought about by the donor.

Another cause of energy losses in the dye laser is the transition of the stimulated dyestuff into the triplet state. This is particularly the case when the dyestuff reabsorbs its own fluorescence emission and occupies higher triplet levels. This problem can be countered by the addition of triplet quenchers. These are compounds which themselves convert into the triplet state and change the excited dyestuff from the triplet state back to the ground state so that the compound can then return, through the absorption of energy, into the S_1 excitation level that is capable of fluorescence. By linking a triplet quencher with a fluorescent dyestuff, Lüttke and Schäfer¹¹ were able to achieve a spectacular increase in the efficiency. The previously mentioned oxazole compound again served as the fluorescent dyestuff, and trans-stilbene as the triplet quencher. Fig. 9 shows that the fluorescence of trans-stilbene corresponds almost perfectly to the absorption of dimethyl POPOP.

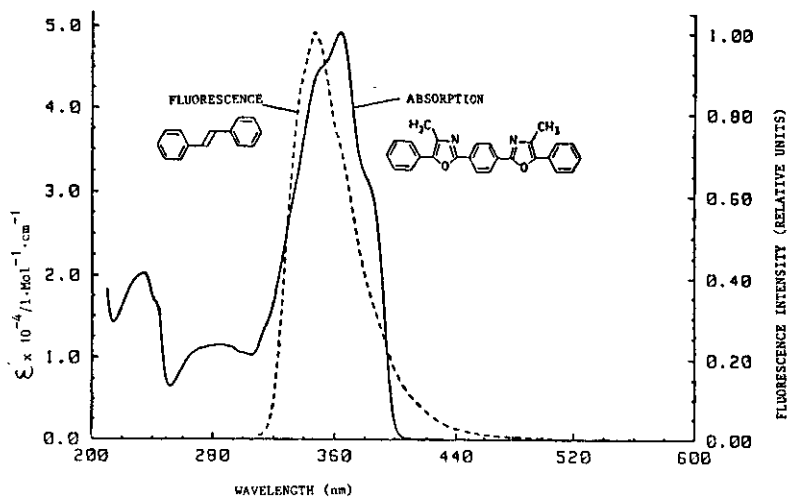


Fig. 9

The following energy diagram (fig. 10) depicts the triplet energy transfer.

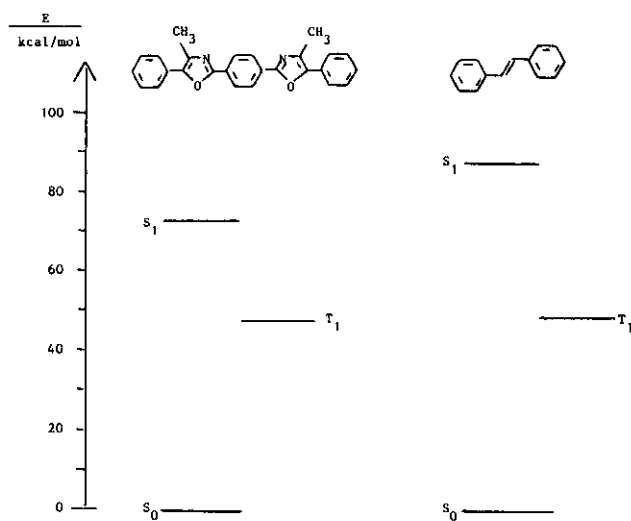


Fig. 10

The exceptional increase in the efficiency on coupling both the compounds is clearly illustrated in fig. 11.

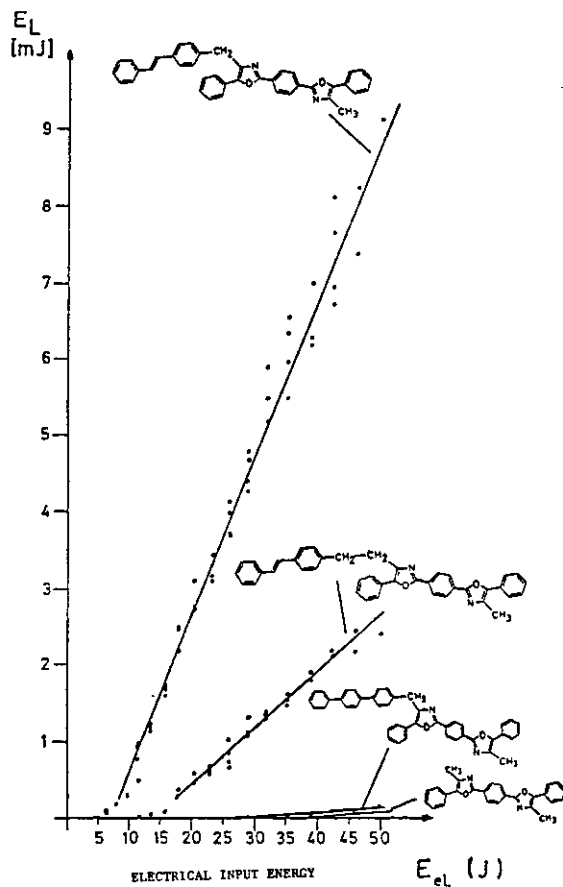
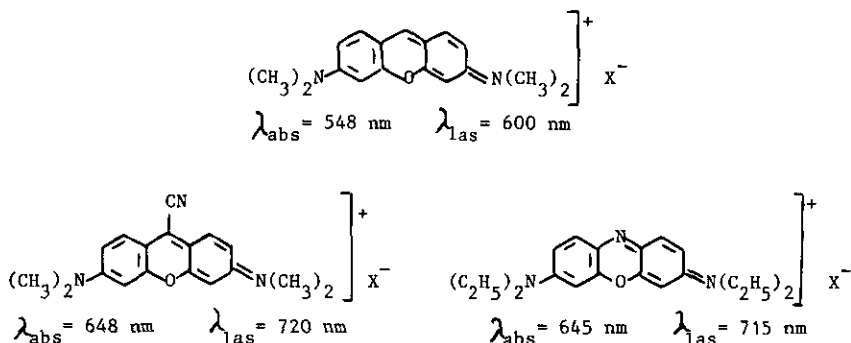


Fig. 11

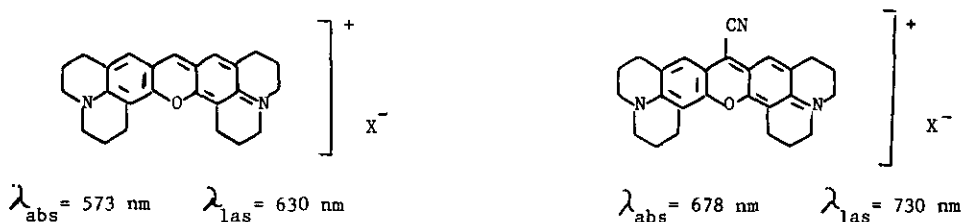
The optimum distance is achieved only by coupling the compounds over a methylene bridge. Coupling over an ethylene bridge has a far lower level of effectiveness, though still well above that of the bifluorophorous laser dye of terphenyl and the oxazole compound. Although the increase in effectiveness brought about by linking the terphenyl and dimethyl POPOP is clearly evident compared with these effects, it is still fairly modest.

The aim of our work was to study the influence of cyano substitution on the fluorescence properties of xanthene, carbopyronine and coumarin dyestuffs. Xanthene dyestuffs can be regarded as monomethine dyestuffs that have been ring-closed with oxygen. From the electron gas model of the methine dyestuffs, it was expected that a major bathochromic shift would occur by replacing the central methine group with a chain member of higher electron affinity. Nitrogen could be used as the ring member; during the changeover from the xanthene dyestuffs to the oxazine dyestuffs,

we observe - in line with theory - a considerable bathochromic shift. Cyano substitution on the central carbon atom has a similar effect.



The fluorescence quantum yield with the xanthene dyestuffs is highly dependent on temperature. At room temperature for the non-substituted xanthene dyestuff, it is 56 %, while at -20°C it rises to 90 %. The cyano-substituted xanthene dyestuff has a fluorescence quantum yield of 50 % at room temperature in dichloroethane, and only 16 % in ethanol. If we prevent the rotation of the alkyl groups on the terminal nitrogen atoms by ring-closure rigidizing, the fluorescence quantum yield at room temperature can be raised to 100 %. The bathochromic effect due to the ring closure is 30 nm. The introduction of the cyano group again brings about a strong bathochromic effect. The fluorescence quantum yield nevertheless falls to 39 % in dichloroethane, which means that different types of quenching mechanisms must be possible by the cyano group. As expected, the fluorescence quantum yield can therefore not be raised by cooling.



The following diagram (fig. 12) shows the fluorescence and absorption curve of the cyano-substituted dyestuff.

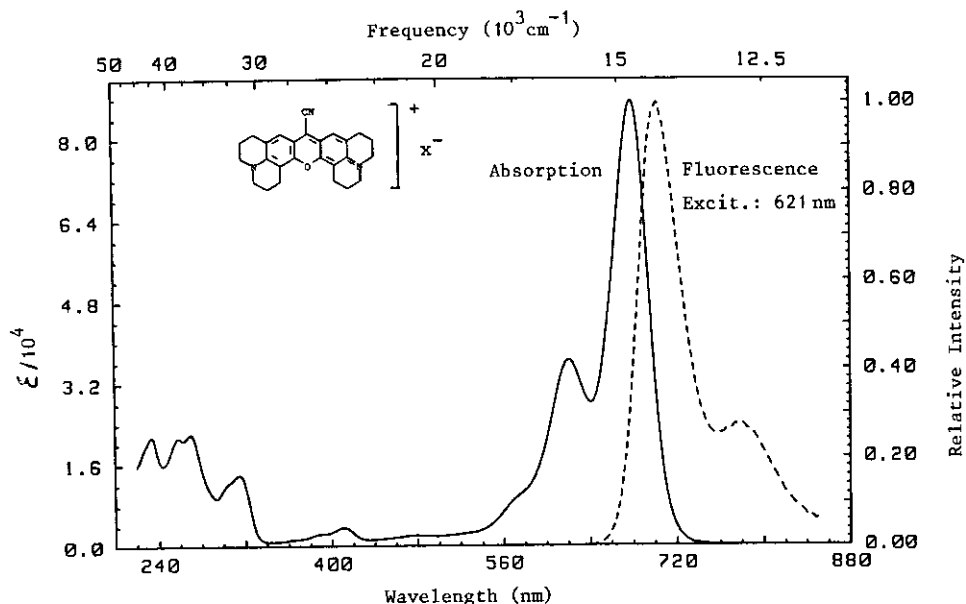


Fig. 12: Absorption and fluorescence spectra in methanol

Nevertheless, this dyestuff represents a considerable advance since, as the tuning curve shows (fig. 13), it has a very broad tuning range and particularly

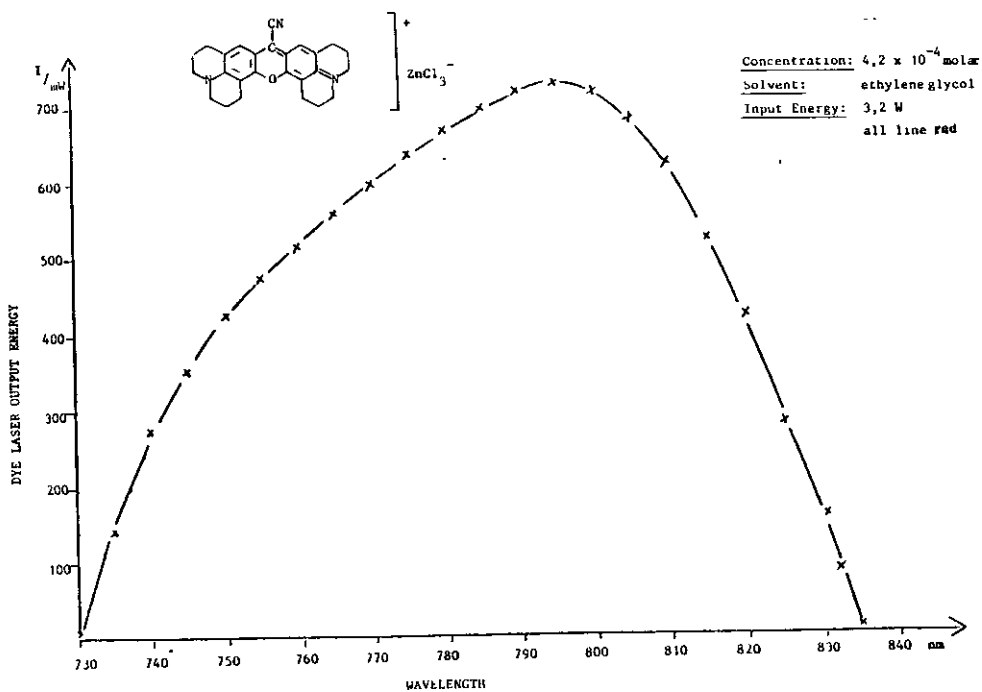


Fig. 13: Tuning curve

efficient in the range between 800 and 825 nm, which has so far been weakly represented. For the introduction of the cyano group, sodium cyanide is first added to the dyestuff dissolved in dimethylformamide and the resultant dihydro compound oxidized by the addition of bromine. This process gives far purer products than oxidation with iron chloride in aqueous solution.

Our next aim was to shift the tuning range even further into the long-wave field using ring-closed methine dyestuffs. The best prospects for this were offered by cyanization of carbopyronine, a dyestuff obtained from 3-propenyldimethylaniline by reaction with the condensation product of dimethylaniline, formaldehyde and sulphanic acid, ring closure in concentrated sulphuric acid and oxidation with lead oxide.¹² Compared with the corresponding xanthene dyestuff, the absorption maximum is shifted 60 nm into the long-wave field. The absorption maximum of the cyanized dyestuff is 711 nm, in other words 30 nm further in the long-wave region than the ring-closed cyanized xanthene dyestuff.

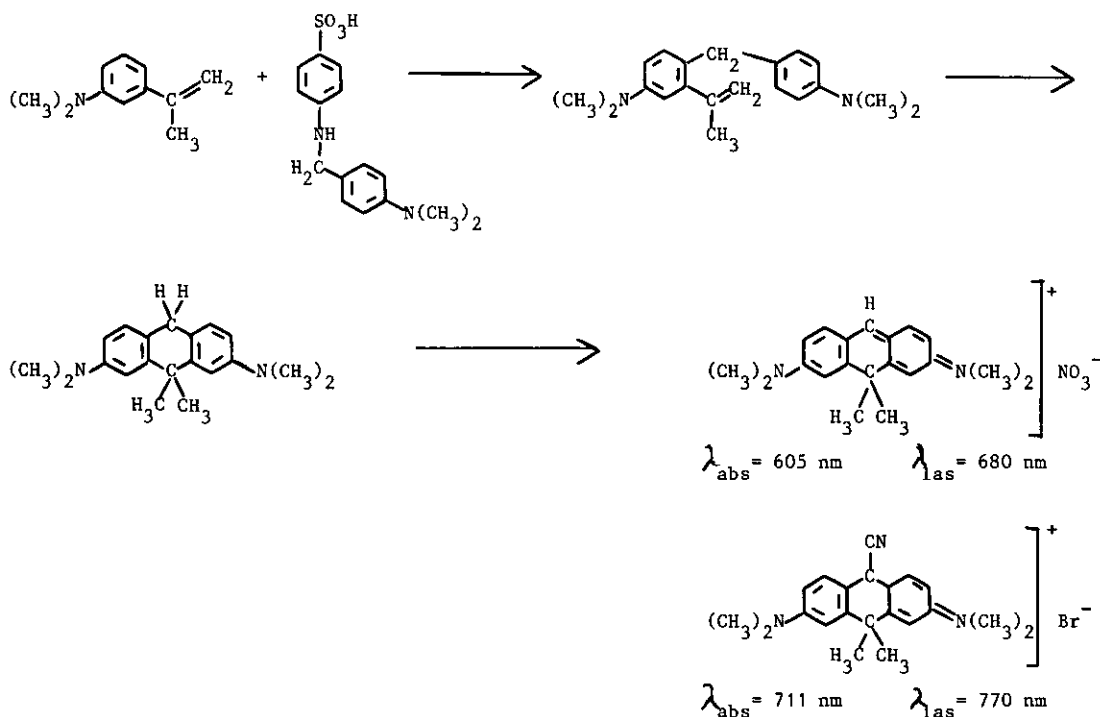


Fig. 14 shows the absorption and fluorescence curve of this dyestuff.

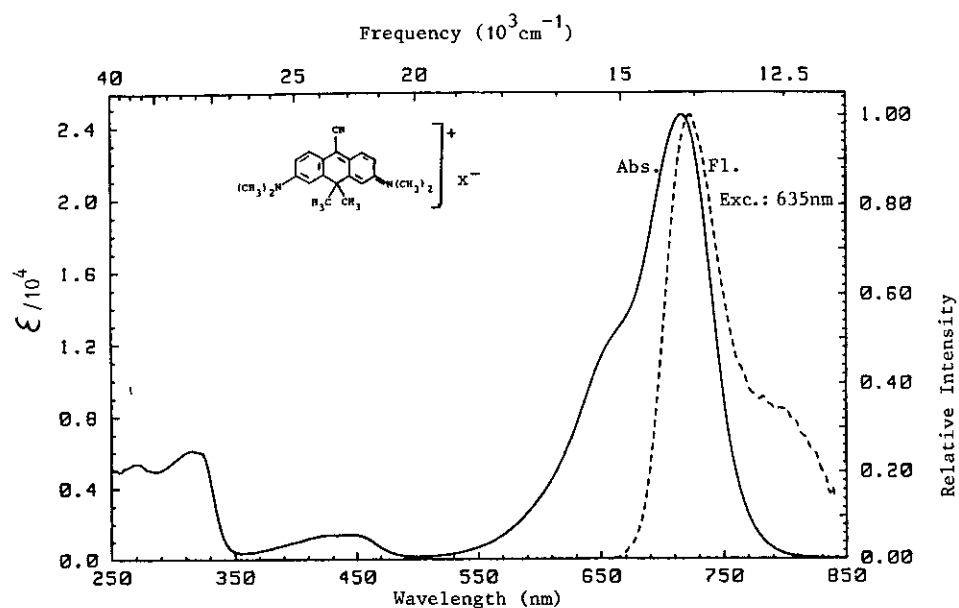


Fig. 14: Absorption and fluorescence spectra in methanol/acetic acid

However, it was not possible to extend the tuning range beyond the 830 nm that had already been reached, since the carbopyronin dyestuff has much narrower tuning range than the xanthene dyestuff. Its maximum laser power is also surprisingly low (fig. 15).

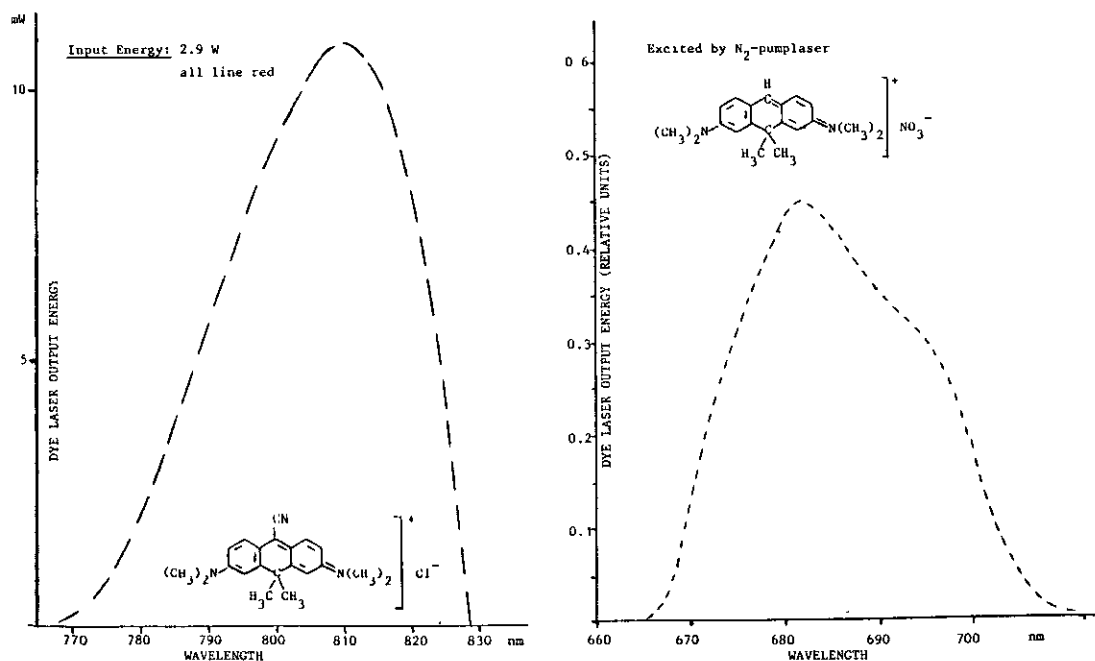
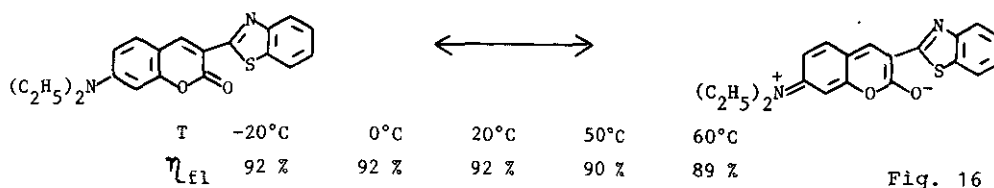


Fig. 15: Tuning curves

The fluorescence quantum yield of the coumarin dyestuffs, unlike that of the xanthenes dyes, is not dependent on temperature. This means that rotation of the substituents on the amino group is also restricted at room temperature. A possible reason for this is that coumarins change into the betaine form in the excited state (fig. 16).



The corresponding ring-closed coumarin dyestuff has an insignificantly higher quantum yield of 94 %. The ring-closed dyestuffs nevertheless have a much higher laser power. The dye laser was pumped with an excimer laser, whose excitation energy was 13 mJ/pulse. An energy conversion in the order of 10 % is thus achieved (fig. 17).

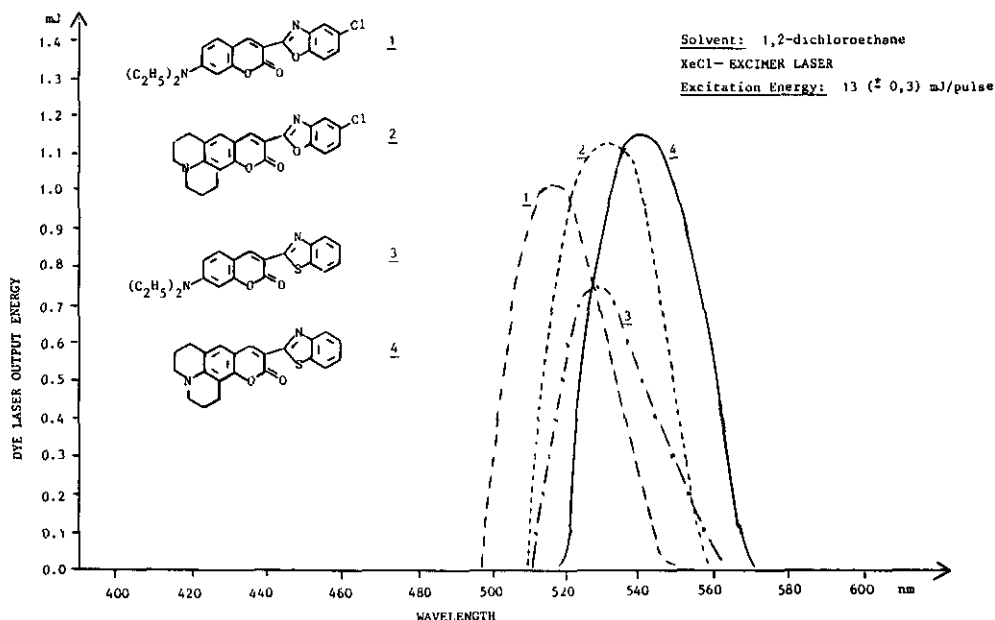


Fig. 17: Tuning curves

By the addition of sodium cyanide and subsequent oxidation with bromine, these four dyestuffs are substituted in the 4-position by the cyano group.¹³ A study of these dyestuffs in the laser produced results that exceeded all expectations (fig. 18). It was found that, in the case of the ring-closed compounds, there was only a very slight decline in the output energy. The benzoxazole dyestuff could be tuned in the range between 610 and 710 nm over an extremely broad wavelength range. The

corresponding non-ring-closed dyestuff, with its tuning range from 580 - 650 nm, lies in the range of the present standard dyestuff from the pyrane class, the DCM. The ring-closed benzthiazole dyestuff can, from 630 - 710 nm, still be tuned over an amazingly broad wavelength range with a high output power; whereas the corresponding 3-benzthiazolyl-4-cyano-7-diethylaminocoumarin dyestuff has a much lower efficiency level. The surprising point about the laser output energy curve for this dyestuff is its minimum at 620 - 640 nm. This anomaly points to a transition into higher singlet states, as a result of which the energy for fluorescent radiation is no longer available in this range.

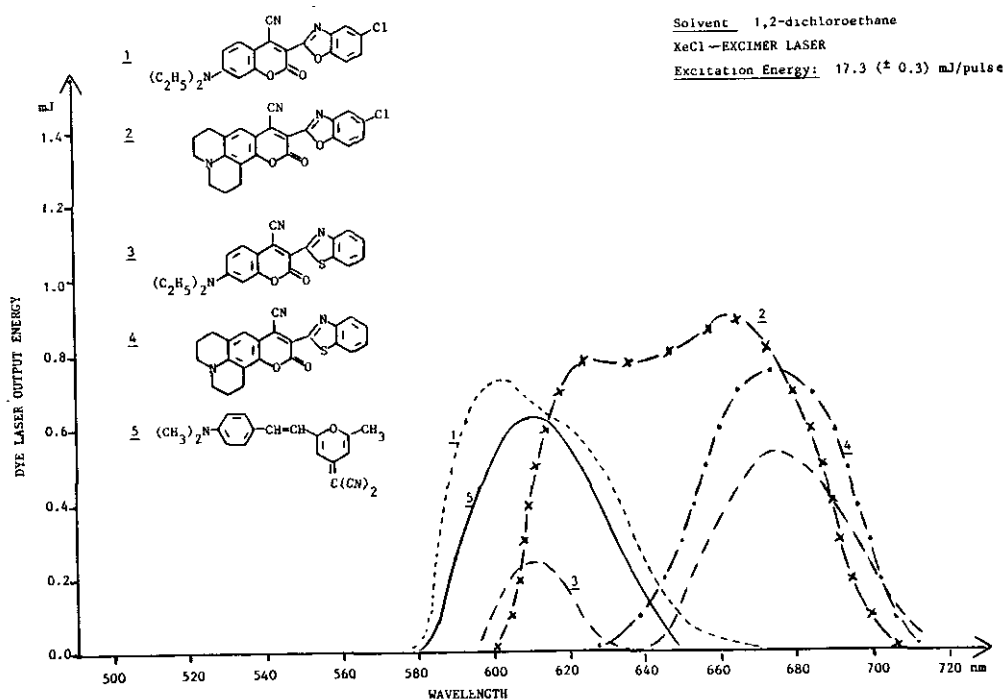


Fig. 18: Tuning curves

The same anomaly was observed in a second group of dyestuffs. The naphthothiazone dyestuff, on excitation with a nitrogen laser of low power, exhibits a very high energy conversion compared with the corresponding naphthoxazon dyestuff (fig. 19). In this range, it exceeds even rhodamine 6G. On irradiation with higher energy density, there is a marked decline in the efficiency. Here, too, a transition into higher singlet levels is a possible cause. Further tests must be carried out in this connection.

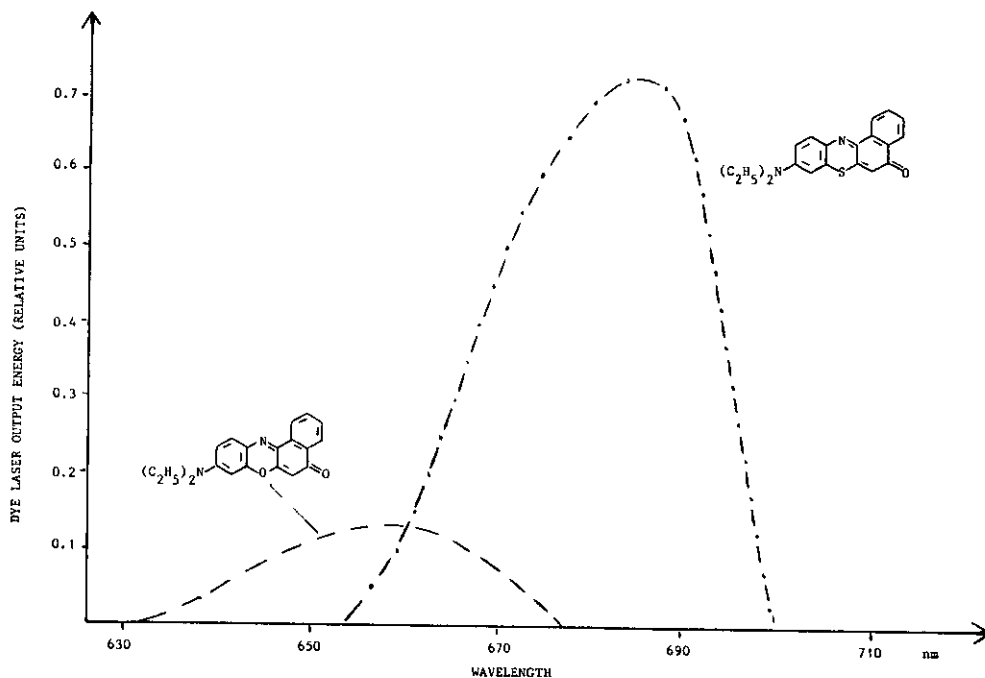


Fig. 19: Tuning curves

An anionic group can be used instead of the amino group as a fluorescence-intensifying donor, not only the phenolate anion, but also the anion of benzenesulphonamide.¹⁴ The anion of 7-hydroxy-3-benzoxazolylcoumarin, in particular, displays a very high energy output on excitation with the xenon chloride excimer laser. The cyano-substituted dyestuffs, on the other hand, are only of very low efficiency (fig. 20), because of low stability in the alkaline medium.

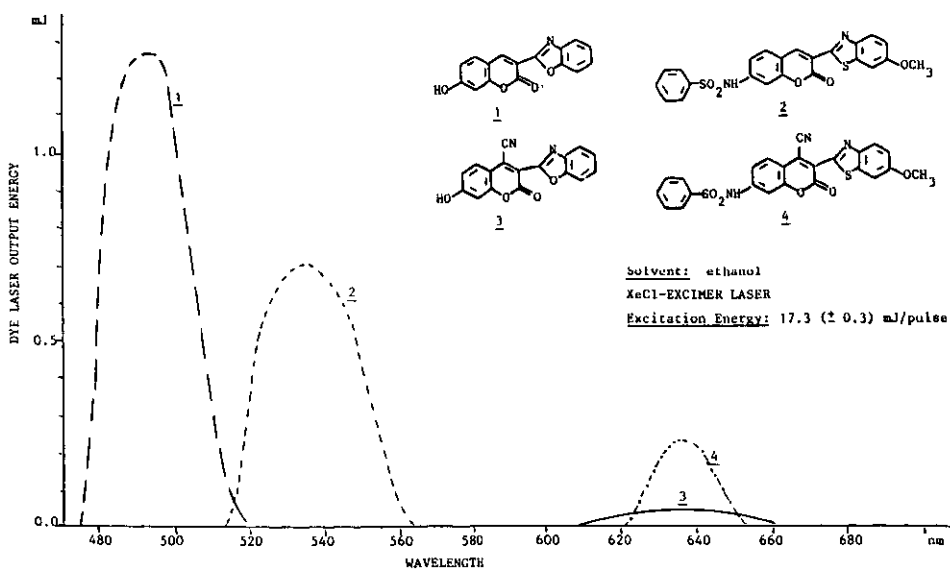


Fig. 20

A further field of application for fluorescent dyestuffs - and one of major technical significance - is that of solar collector. Only with directional radiation is it possible to increase the solar power density using mirrors and lenses. The solar collector makes it possible to use the entire radiation, including the diffuse parts which are of considerable importance in temperate zones. The principle of the luminescent solar collector¹⁵ can be seen from the following drawing (fig. 21):

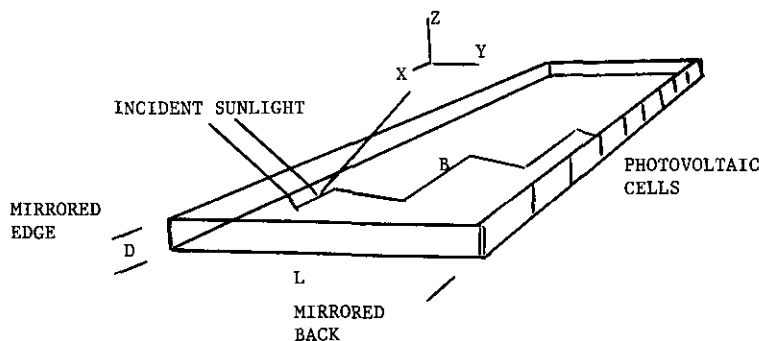


Fig. 21: Planar solar collector

A transparent material, for example polymethyl methacrylate or polycarbonate, is dyed with a fluorescent dyestuff having an intensive absorption in the visible and UV range of the spectrum and also a high fluorescent quantum yield. Solar photons pass through the surface of the plate, are absorbed and release the excitation energy again as luminescence. About 74 % of this luminescence is trapped by total internal reflection in the polymethyl methacrylate with a refractive index of 1.49. Repeated reflections carry the radiation to the edge of the plate, where it emerges and is absorbed by photovoltaic cells. The light amplification is given by the ratio of the plate surface to the plate edge. Assuming a plate thickness of 3 mm, we would thus get an amplification factor of 333 for 1 m². In this way, a very expensive solar cell can be coupled with a low-cost amplification setup to give a system which, all in all, is inexpensive.

A suitable fluorescent dyestuff should have the following properties:

1. As wide an absorption band as possible in order to be able to absorb a large proportion of the available light,
2. A high fluorescence quantum yield so that as little as possible of the irradiated energy is lost by non-radiative processes,
3. As little overlapping as possible of the absorption and fluorescence bands, so that the losses by reabsorption can be kept to a minimum,

4. A high photostability and
5. Good solubility in the selected plate materials.

The following dyestuff from the benzanthrone range has only a small overlapping of the bands (fig. 22):

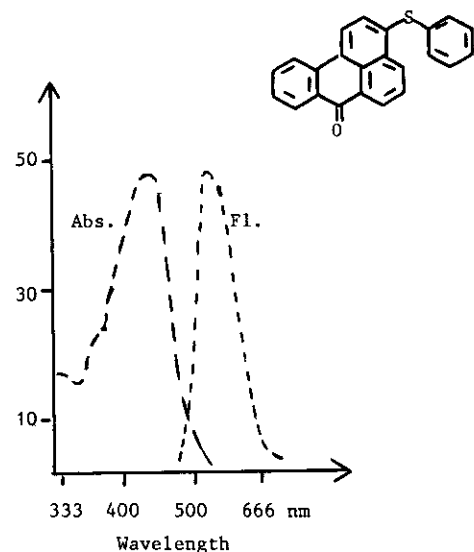


Fig. 22: Absorption and fluorescence spectra in chloroform

This is an advantage, because, in the overlapping area, the luminescence can be reabsorbed by another dyestuff molecule which is still in the ground state. The probability of the reabsorption is greater if the distance of the light to be covered by total internal reflection is large. The reabsorbed light is, in turn, emitted as luminescence and can be absorbed again along the large distance it has to cover through total internal reflection. The result is thus a number of different generations of fluorescent light, with each generation being shifted further into the long-wave range in relation to the previous one. The concentration of the fluorescent dyestuffs in the plate material is 10^{-3} to 10^{-2} molar. The absorption of sunlight increases with increasing concentration, but at the same time the proportion of reabsorbed fluorescent light also increases. Of major importance for the practicability of this process is the lightfastness of the fluorescent dyestuffs. Photochemical decomposition occurs in the excited state. Thus a dyestuff which has returned to the ground state by luminescence will remain undestroyed until the next excitation. In solution, experiments have shown that a photochemical decomposition occurs every 10^6 excitations. Dyestuffs intended for industrial use must be able to

withstand 2000 hours' exposure under the xenon lamp without any significant decline in luminescence. A particularly lightfast group of fluorescent dyestuffs are the perylene tetracarboxylic acid diimides (fig. 23). However, their solubility in plastics is inadequate. Langhals¹⁶ was able to improve the solubility by introducing tertiary butyl groups, thus enabling them to be used in solar collectors.

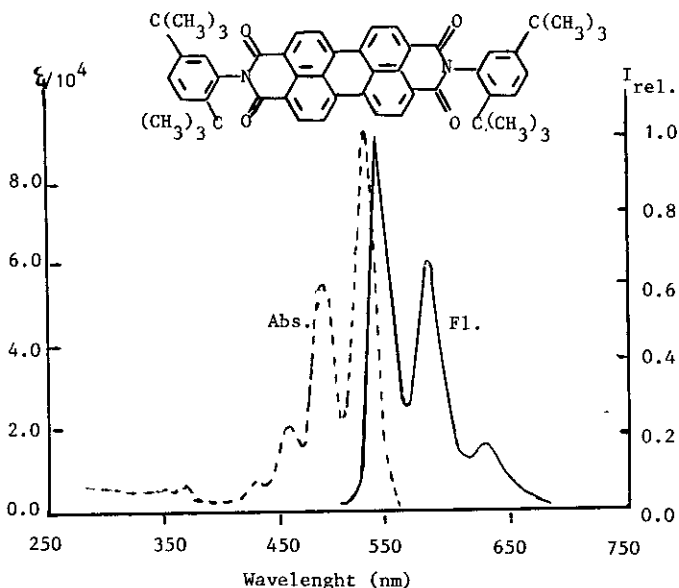
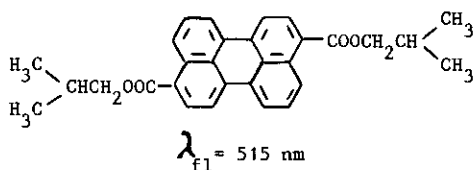
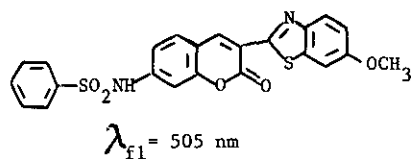
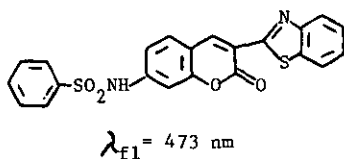


Fig. 23: Corrected UV/VIS-absorption and fluorescence spectra in CHCl₃

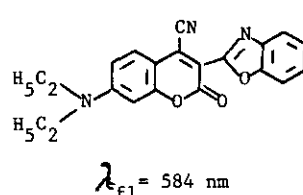
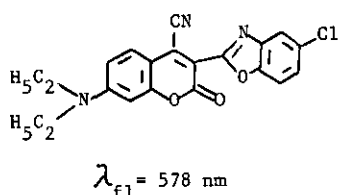
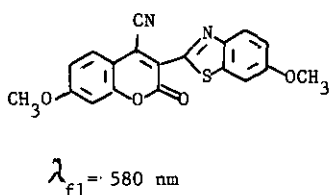
The principle of improving the solubility by means of branched alkyl radicals was applied by Claussen to perylene dicarboxylic acid esters. The dyestuff emits at 515 nm and has good lightfastness.



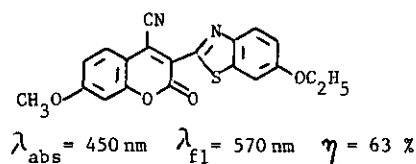
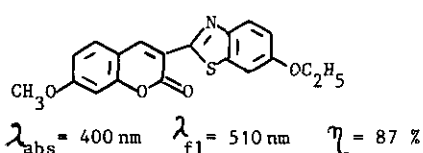
Various outstanding solar collector dyestuffs were found in the coumarin range. The most effective dyestuffs have a heterocyclic radical in the 3-position and differ from one another in the substitution in the 4- and 7-positions. At the short-wave end of the spectral range, there are dyestuffs which are substituted in the 7-position by the benzenesulphonamido radical.¹⁷



The strong bathochromic shift of the absorption and fluorescence maxima by introducing a cyano group to the 4-position has already been dealt with for the laser dyestuffs.¹⁸ Many of these dyestuffs are also suitable for use in solar collectors at a fluorescence maximum of around 580 nm.



From what has been expounded so far, we could conclude that the same dyestuffs are suitable for use in dyestuff lasers and in solar collectors. However, this is not always the case. The dyestuffs having the formulae



are suitable for use in solar collectors. Their fluorescence quantum yield also leads us to expect this as it is in the order of other laser and solar collector dyestuffs. Nevertheless, it is not possible with these two dyestuffs to produce any laser radiation on excitation with the xenon chloride excimer laser. The possible reason for this is a slight transition of these dyestuffs to higher singlet levels. This can prevent the high occupation density of the S_1 level, which is necessary for laser radiation. The high energy density of the laser excitation is thus the distinguishing factor between use in dyestuff lasers and use in solar collectors. Here, too, it is evident that there are still a number of questions to be answered in this fascinating field of work.

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