

PHOTOCHEMICAL GENERATION OF STABLE FLUORESCENT COMPOUNDS (PHOTOFLUORESCENCE)

ARNOLD ZWEIG

*American Cyanamid Company, Central Research Division, Stamford,
Conn. 06904, USA*

ABSTRACT

The mechanistic insights afforded by investigations of photochemically-generated stable fluorescent compounds are examined. Examples of the types of such photofluorescent processes found in the literature are reviewed. The photochemical self-quenching rearrangement of furyl chromones, wavelength-dependent rearrangement of azirines, halogen-dependent cycloelimination from halophenylnaphthalenes and decarboxylation-decarbonylation of 1,2-dicarboxylic anhydrides are examined as photofluorescent systems. The efficient photoelimination of carbon monoxide and carbon dioxide from thermally stable 1,4-dicarboxylic anhydrides is reported and mechanistic information obtained from the formation of fluorescent products in this process is described.

The photochemical generation of stable fluorescent products from non-fluorescent precursors, a process which we have termed photofluorescence, has been casually noted in the literature for many years. There appears to have been no previous deliberate effort to create and examine this phenomenon, although there are very good reasons for doing so. I would first like to mention briefly some of the more cogent reasons and then proceed to examine the photochemistry that our efforts in this area have led to.

The most fundamental reason for photogenerating fluorescent materials is to use them as a probe for examining the potential energy surface of the photochemical transformation. Professor Förster described his studies on diabatic and adiabatic processes in photochemistry¹ to the Third IUPAC Symposium on Photochemistry. He raised the question as to how molecule A is transformed photochemically to molecule B (*Figure 1*). Does deactivation of the electronic excitation take place in the reactant (as in 1) or in the product (as in 2) or in between (as in 3). Observation of characteristic emission from the fluorescent product excited state achieved through absorption by the precursor is good evidence for process 2 deactivation. We will explore the experimental requirements for such observations and report our results further on, but before that I'd like to go on to the applied areas and mention the photo-imaging possibilities with stable photofluorescent systems.

We are well aware that under most circumstances a fluorescent test can

A. ZWEIG

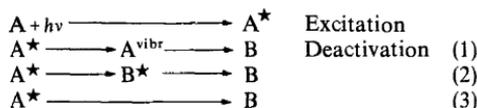


Figure 1. Alternative pathways in the photochemical conversion of A to B

detect orders of magnitude less material than a colour test and this is why fluorescent tags and tracers are widely used in trace analytical applications². Indeed it is a common laboratory practice to examine a chromatographed reaction mixture with an ultra-violet lamp to detect separating fluorescent products. It should be evident that an efficient photochemical process that generates a stable and efficient fluorescent product from a non-fluorescent precursor will have an effective speed orders of magnitude greater than an equally efficient photochemical process that yields even a deeply-coloured product only detectable by differences in absorption. It should not be surprising, therefore, that as seen in *Figure 2*, the first photofluorescent imaging material³ exhibited practical sensitivities comparable to that of photopolymer systems and much faster effective speed than that of non-polymerizing organic imaging materials, but, of course, still five orders of magnitudes lower than that of high speed silver photographic film.

System	Practical exposure microjoules/cm ²	Relative sensitivity
Silver halide, Tri-X	0.001	3×10^7
Photofluorescer	100	300
Photoplastic, 216 film	150	200
Dry silver	800	43
UVI film	5000	6
Photochromic	30000	1
Kalvar	400000	0.075
Diazo	800000	0.033

Photofluorescer data from A. Zweig, Symposium III on Unconventional Photographic Systems (1971). Other data from J. E. Bigelow, 9th National Symposium on Information Display, May 1968.

Figure 2. Relative sensitivity of various films

Practical exposure as used in *Figure 2* refers to the exposure to radiation per unit area required to differentiate between exposed areas and background after suitable development. The high speed of silver halide film as compared to organic systems is due to the development step where the effect of only a few quanta makes a micron size grain develop. Professor Bird has pointed out that because several photons are needed to make a grain developable and because of other losses, the detective quantum efficiency of even the most sensitive silver halide films is only of the order of one to two per cent⁴. He has suggested how suitable organic photofluorescent materials could be utilized to capture and display an image with greater sensitivity than that available from silver halide film⁴. In his concept, as illustrated in *Figure 3*, the photofluorescent material captures the image in a molecular transformation in the

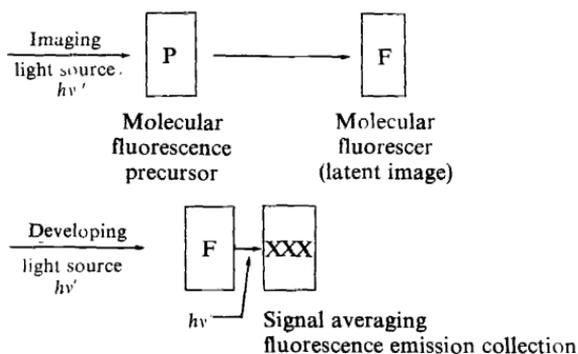
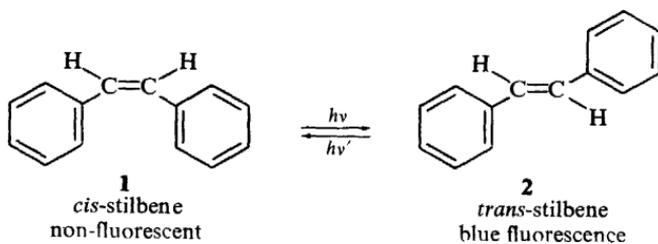


Figure 3. High speed photography with photofluorescent materials

first step and then in a developing step the presence of fluorescing molecules is detected and amplified by a developing beam of light. The development is effected by employing the initially produced stable fluorescer as a sort of catalyst which reveals its presence through the performance of its function. Thus conceptually, if not yet in practice, photofluorescent systems offer the opportunity of even greater sensitivity than silver halide-based materials.

One of the first descriptions of the photolytic generation of an identified fluorescent product was made by Lewis, Magel and Lipkin⁵, who observed development of a blue fluorescent product when non-fluorescent *cis*-stilbene (1) was photolysed. The photolytic change induced was shown to be the isomerization of 1 to *trans*-stilbene (2). The authors utilized this photolytic



generation of a fluorescent product to help clear up the existing confusion regarding this *cis-trans* isomerism.

Cis to *trans* photoisomerisms are an important class of photofluorescers. In Figure 4 we have listed some familiar examples such as substituted stilbenes⁶, indigo dyes⁷, and β -styryl compounds⁸, as well as the remarkable photoconversion of a non-fluorescent all *cis* 1,2,4,7-tetraphenylcyclooctatetraene to a fluorescent *trans* containing isomer⁹, illustrating the apparent thoroughness of the relationship of *cis-trans* photoisomerization to photofluorescence. Despite this ubiquity, these are not the best reactions to choose for an initial detailed investigation of the photofluorescence process because: (1) there are relatively small differences in absorption spectra between product and precursor, (2) under some conditions the *cis* isomer becomes fluorescent^{9a}, and, (3) photoreversibility, modest photoefficiency and occurrence of side reactions cloud attempts at quantitative evaluation.

There are certainly many other types of reactions described in the literature

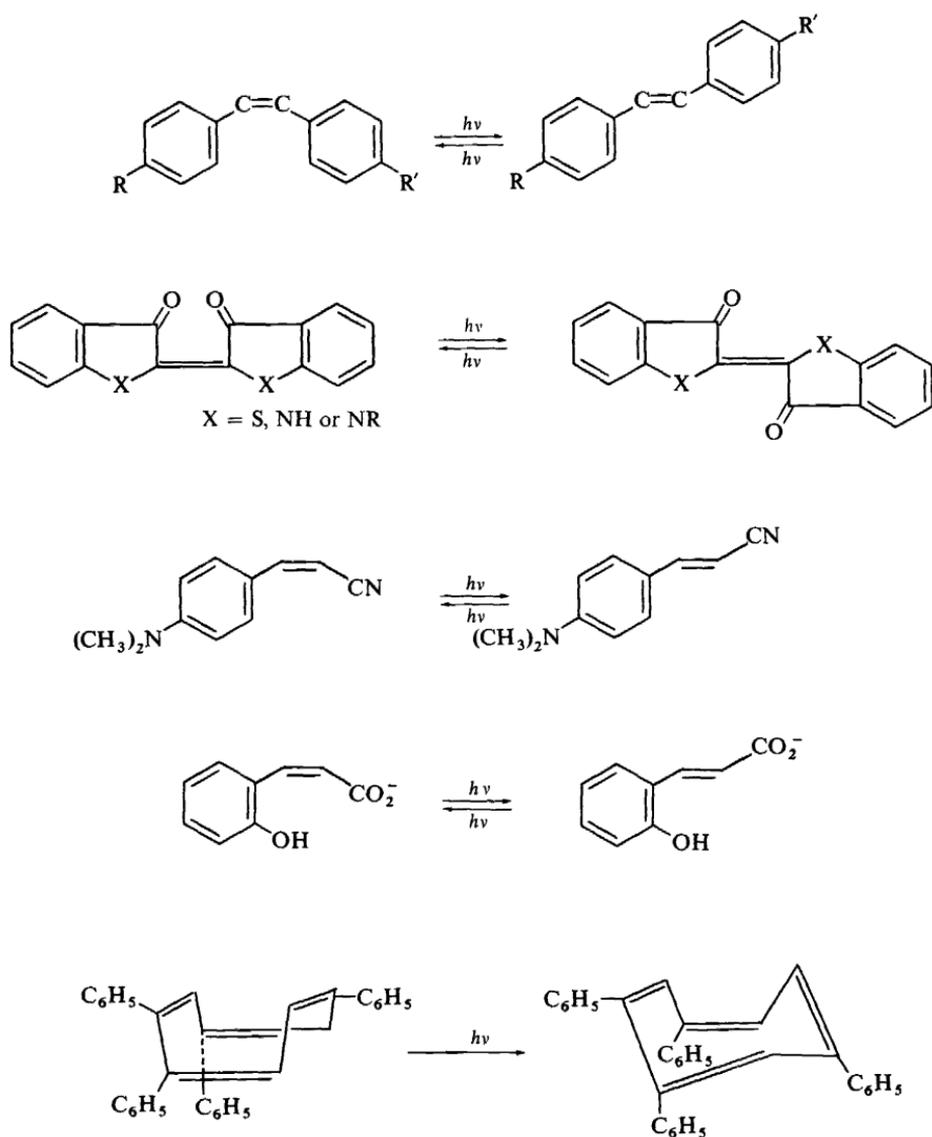


Figure 4. Photofluorescent *cis-trans* photoisomerism

where stable fluorescent products are photogenerated. Examples can be found in most of the broad classes of transformations that have been established. For a frame of reference, I've listed in *Figure 5* some of these classes and have selected in each an example to illustrate the point. As in the case of *cis-trans* isomerisms, the fact that the product may be fluorescent while the precursor is not, has, except in some very specialized situations, not received more than perfunctory notice. One exception to this is the photodimerization process to yield stable fluorescent monomers. Here Förster¹ reported that anthracene is not photoproducted in the fluorescent state in greater than

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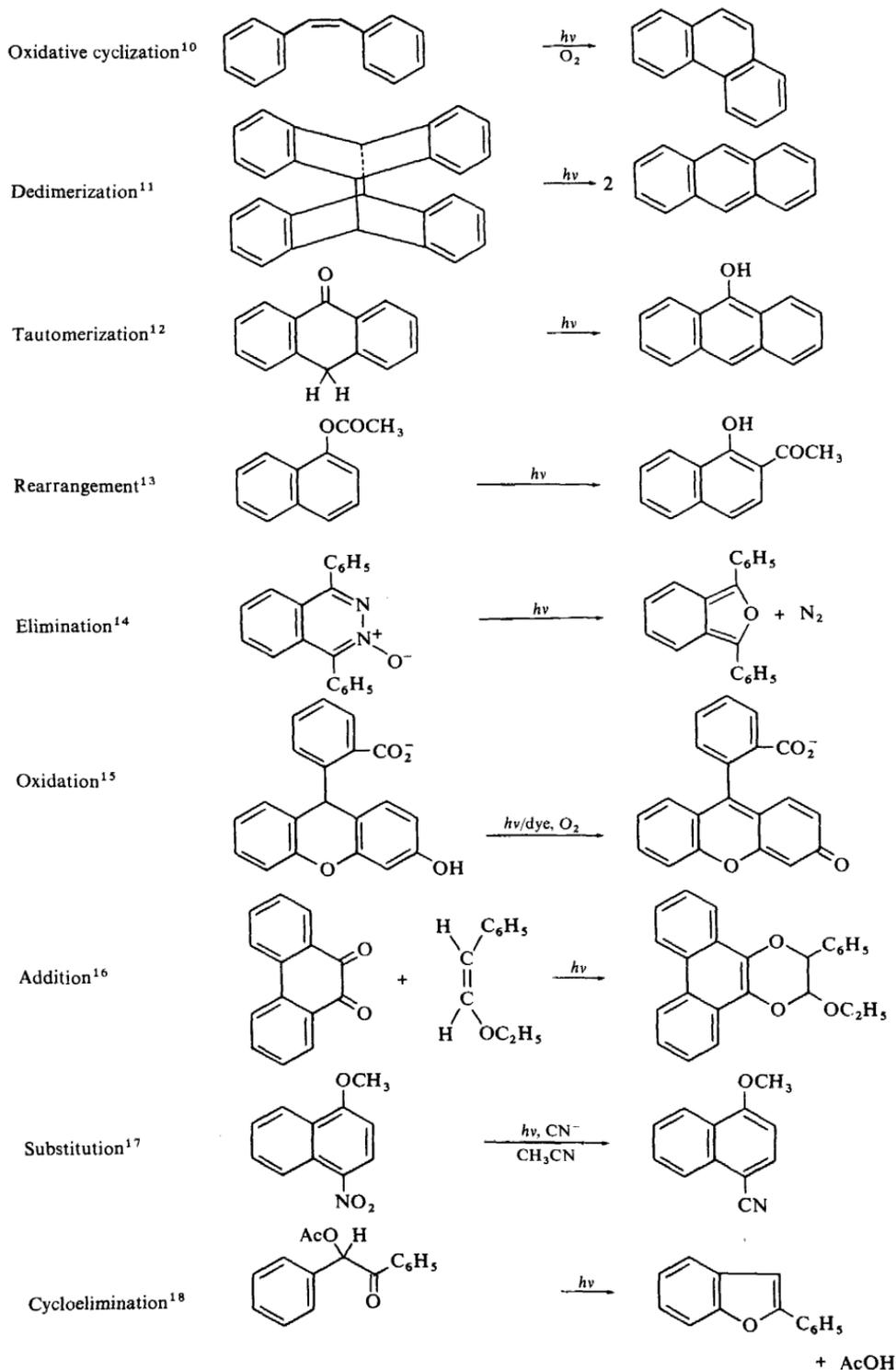


Figure 5. Photochemical reactions generating stable fluorescers

one-hundredth of one per cent. More recently^{1a}, he has reported that di-9-methylantracene directly photoproducts 9-methylantracene emission with a fluorescence quantum yield of 0.04 ± 0.005 per cent.

Our own awareness of photochemically generated stable fluorescers resulted from studies of photochemical rearrangements of 3-aryloxy-2-(2-furyl)chromones such as the 3-*p*-anisoyl compound shown in Figure 6¹⁹. We

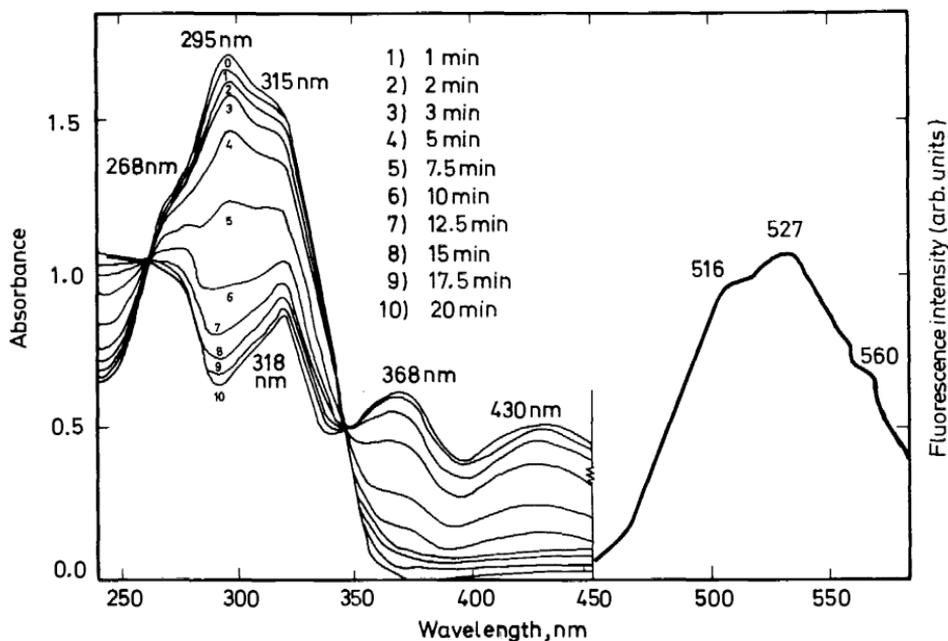
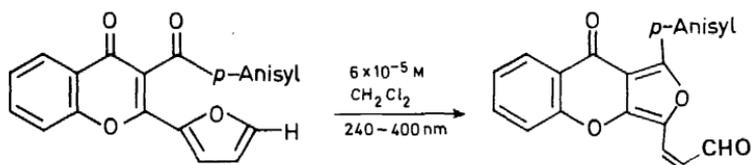


Figure 6

found that the furyl chromone on the left which is a non-fluorescent compound is smoothly converted by irradiation in dilute degassed solution to produce the isomeric 1-arylfuro[3,4-*b*]chromone-3-acrolein on the right. The starting material absorbs strongly at 295 nm, but the product does not. As the reaction proceeds, absorption in this region decreases. At longer wavelengths the product has greater absorption than the precursor with maxima at 368 and 430 nm. It has an orange colour, and exhibits intense green fluorescence ($\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 527 nm; $\Phi = 0.40$)²⁰. Unexpectedly, when this reaction was run at higher concentrations, the efficiency of the conversion decreased drastically. Investigation showed that the concentration dependence was a result of the photolysis proceeding through the lowest triplet of the reactant which was efficiently quenched by the product. In the course of establishing this

mechanism, spectroscopic studies were made at different concentrations and detection of the product at low conversions was necessary. The fact that the product is an intense fluorescer led to its ready visual detection at 10^{-8} M, a far lower concentration than could be measured by absorption in the equipment employed. Although the detection of this fluorescence proved unnecessary for establishing the mechanism of this photorearrangement, it brought our attention to the relatively unexplored subject of photolytically generated stable fluorescers.

If it is intended as a probe for mechanistic studies, it is desirable that a photofluorescent compound shall have a combination of characteristics. Although individually these are self-evident, there are several of them and since they haven't been listed before, they are summarized in *Figure 7*. The

Precursor

- Activated by wavelengths not strongly absorbed by product
- Non-fluorescent
- Chemical and thermal stability

Photoconversion

- Efficient (high quantum yield)
- Effective (no deleterious processes)

Product

- Activated by wavelengths not absorbed by precursor
- High fluorescence efficiency
- Chemical and thermal stability

Figure 7. Photofluorescer characteristics

furylchromone in *Figure 6* has all the initial characteristics necessary for such a material. It is non-fluorescent, reasonably stable, and absorbs strongly in the 300 nm region where its photoproduct, the furochromone does not. The photoconversion of the furylchromone is, as mentioned earlier, not efficient. The quantum yield is at best four to five per cent and the phototransformation, proceeding as it does through the triplet, is sensitive to oxygen and other quenchers. The furochromone product has several of the characteristics needed for mechanistic studies on photofluorescent systems. It can be activated by wavelengths above 400 nm that are not absorbed by the precursor. Its fluorescence emission is well in the visible and its fluorescence efficiency is fairly high (40 per cent).

Another photochemical reaction where the product is an efficient fluorescer is the wavelength-dependent photogeneration of 2,5-diaryloxazoles²¹. These oxazoles are not only highly efficient fluorescers, but also possess the exceptional environmental stability that allows their employment as scintillators for detection of ionizing radiation²². The isomeric 2-aryl-3-aryl-1*H* azirines are converted to these oxazoles with moderate (up to 30 per cent) quantum efficiency when exposed to short wavelength irradiation. In the example studied in greatest detail²³, shown in *Figure 8*, 2(1'-naphthoyl)-3-phenyl-2*H* azirine is converted to 5-(1'-naphthyl)-3-phenyloxazole and 5-(1'-naphthyl)-3-phenylisoxazole in a 3:1 ratio when irradiated in its short wavelength absorption band (λ_{\max} , 238 nm). Excitation of this azirine in its long wavelength absorption band (λ_{\max} , 304 nm) produced only the isoxazole

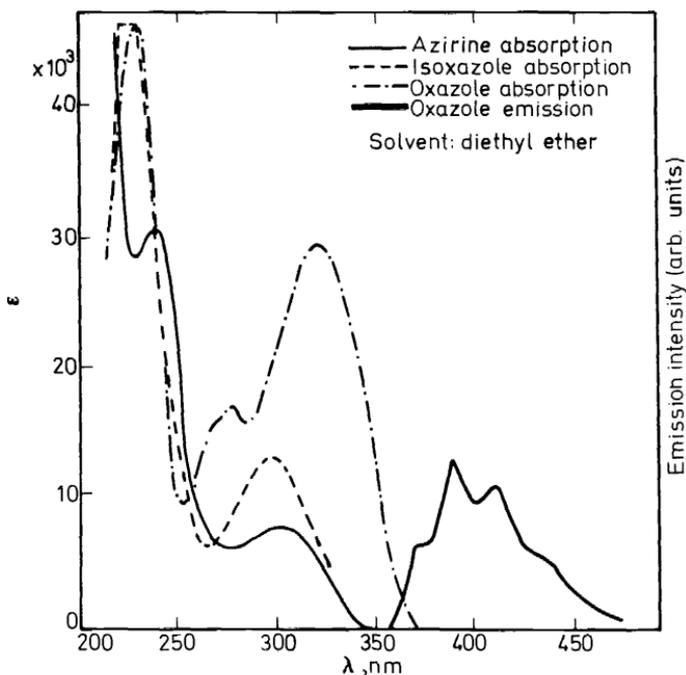
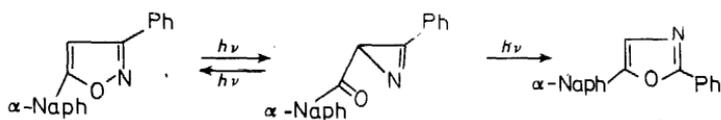


Figure 8

which is also photolabile. The photolysis of this azirine is an unusual case where two rearrangements to give significantly different products proceed from different excited states of the same molecule. The photogeneration of oxazoles is not one in which the photofluorescent phenomenon can be studied with facility because of the close similarity of the absorption spectra of precursor and product, and the reversibility of the isoxazole phototransformation.

Another example of a potential photofluorescent system that had been under investigation in our laboratory was one concerned with the photogeneration of fluoranthene²⁴. The name fluoranthene of course is derived from its strong blue fluorescence in ultra-violet light. We found (Figure 9) that fluoranthene can be photogenerated by irradiation of 1-(*o*-chlorophenyl)naphthalene²⁴. The quantum efficiency is 500 times that of other aryl chlorides, but its absolute value (0.4 per cent) is not as large as desired. The corresponding iodide undergoes the initial photocleavage step much more efficiently (> 12 per cent) but does not yield fluoranthene because the iodine atom co-product is not sufficiently strong an oxidant to oxidize the intermediate aromatic radical²⁴.

Reports in the literature have stated that photolysis of 1,4-diphenyl-1,3-cyclohexadiene-5,6-dicarboxylic anhydride (m.pt 158°C) gives *p*-terphenyl in

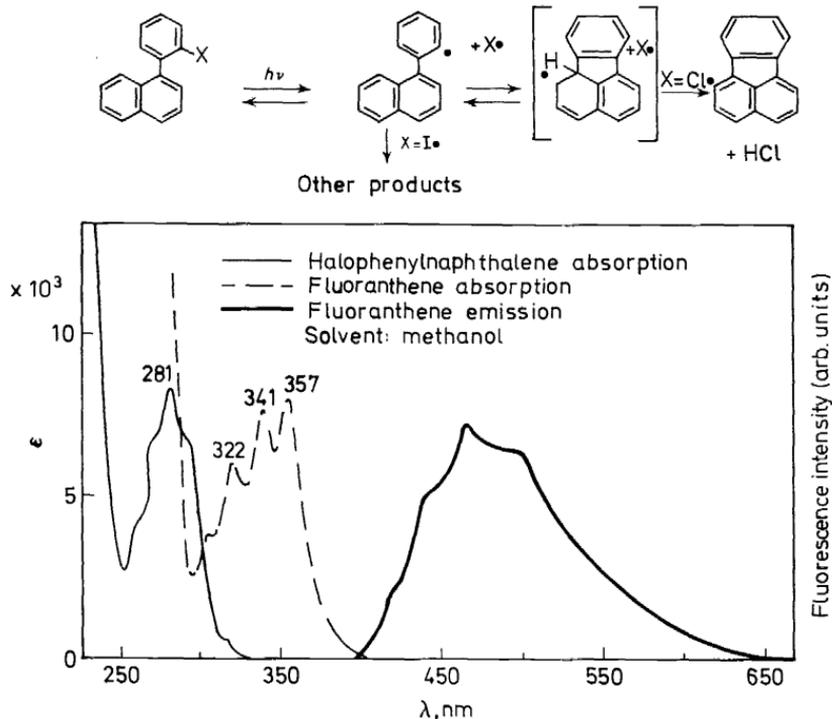


Figure 9

high yield along with carbon monoxide and carbon dioxide²⁵. *p*-Terphenyl is another stable efficient fluorescer used as a scintillation counter for ionizing radiation²². Examination of the published spectra of the anhydride fluorescer precursor and the fluorescent photoproduct, shown in *Figure 10*, reveals that instead of a bathochromic shift in absorption as a result of the photolysis, there is a hypsochromic shift indicating that S_1 for the fluorescent product is higher than S_1 of its precursor. This means that there is insufficient energy in the excited precursor for the product to be generated in its fluorescent excited state.

The lack of fluorescence in this thermally stable precursor of an efficient hydrocarbon fluorescer attracted our attention as a possible starting point for the deliberate design of a photofluorescent system having the characteristics described in *Figure 7*. We therefore decided to investigate further the structural and electronic requirements for photolysis of dicarboxylic anhydrides.

A previous study^{25c} had reported that 1,2-diphenylsuccinic anhydride (the stereoisomer had not been specified), as shown in *Figure 11*, did not undergo photoelimination when irradiated. The study had employed a medium pressure mercury lamp under the same conditions where other 1,2-dicarboxylic anhydrides had given hydrocarbon products in high product yield. It seems evident that this failure could be due to a combination of low lamp output in the region where the diphenylsuccinic

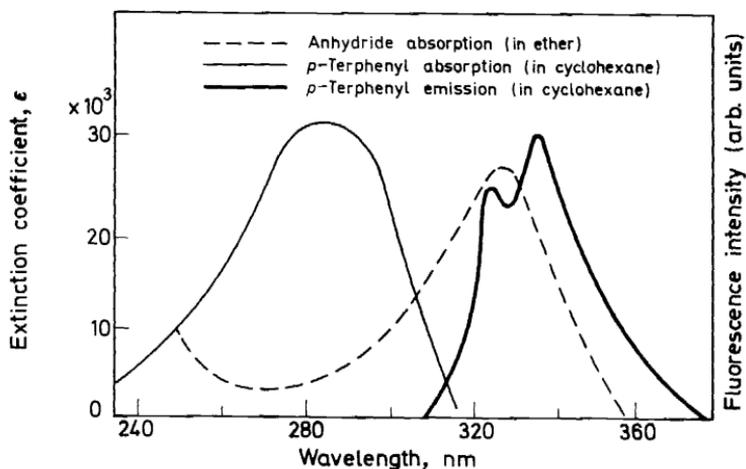
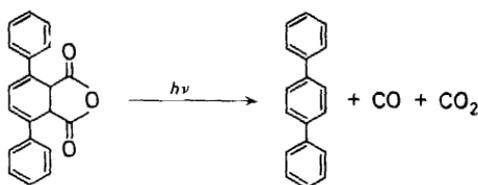


Figure 10

anhydride absorbs and a low extinction coefficient at those wavelengths for this compound, which has only unconjugated phenyl and anhydride chromophores. Evidence indicating that special substituents or configurations are not required for photoelimination from 1,2-dicarboxylic anhydrides was available from the report²⁶ that mercury-sensitized vapour phase photolysis

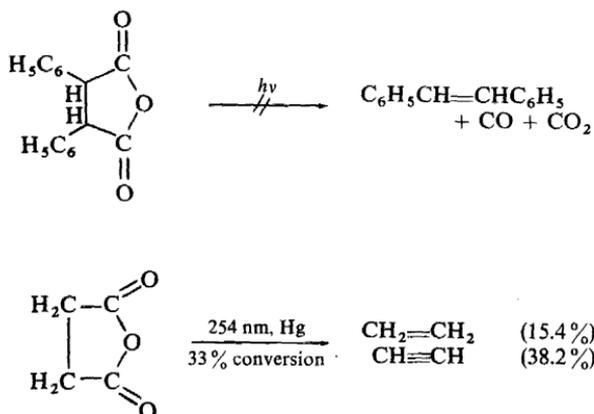


Figure 11. Photolysis of succinic anhydrides

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of succinic anhydride gives about 15 per cent ethylene together with carbon monoxide and dioxide, as well as larger amounts of acetylene.

We found²⁷, as indicated in *Figure 12*, that methylene chloride solutions of both *cis*- and *trans*-1,2-diphenylsuccinic anhydrides did undergo elimination of C_2O_3 when irradiated directly in their short wavelength absorption bands with a low pressure mercury lamp to give *cis*- and *trans*-stilbenes. Because of their efficient photolytic interconversion, the isomeric distribution of the primary photolysis products could not be properly ascertained; however, results with analogous aza-²⁸ and diazasuccinic²⁹ anhydrides were more informative. The expected photoproducts in these cases are anils and azobenzenes which are not fluorescent but contain dyestuff chromophores. On direct irradiation in their absorption bands several examples of these azaanhydrides also photoeliminated the C_2O_3 fragment cleanly and with moderately good quantum efficiency. These photoeliminations could be

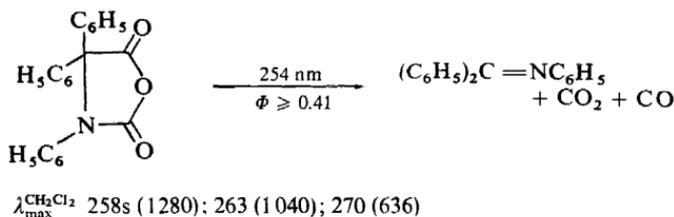
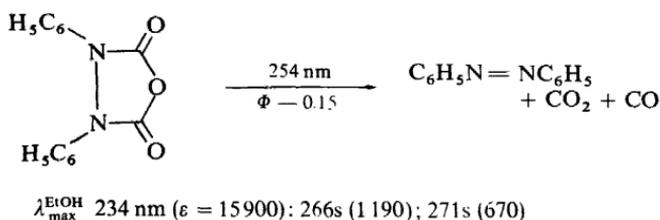
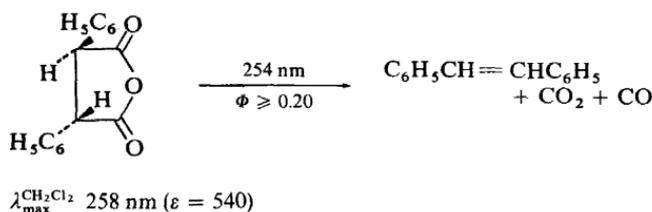
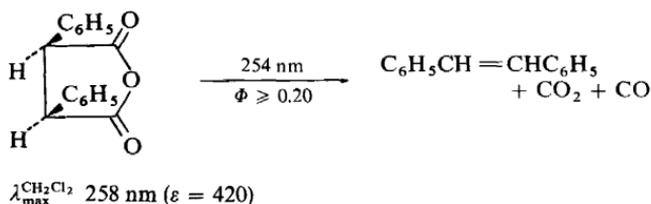


Figure 12. Photoelimination from aryl succinic anhydrides and aza derivatives

sensitized with benzene but not with acetone and could not be quenched by compounds with low triplet states, such as perylene ($E_T = 36$ kcal/mole)³⁰ and thus the evidence indicates that they proceed from an excited singlet state.

Insight into the stereochemistry of the photoelimination of diphenyl-diazasuccinic anhydride could be obtained through analysis of the spectroscopic changes as the elimination proceeds. In hexane solution, irradiated at 254 nm as shown in *Figure 13*, this thermally stable (m.p.t 111°) anhydride

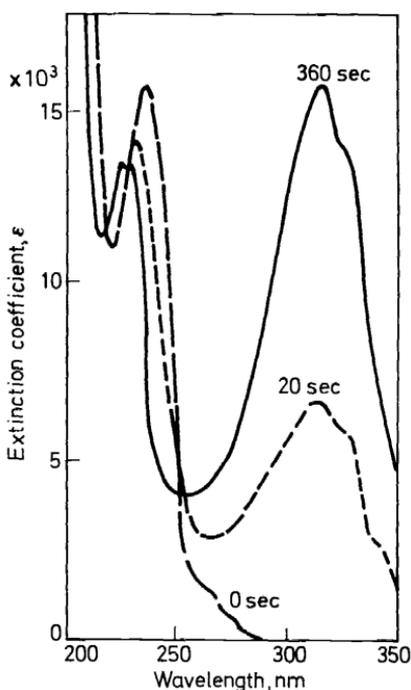
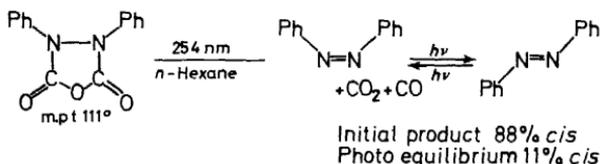


Figure 13

photoeliminates to produce azobenzene which is initially 88 per cent *cis*. Photoequilibration of the product very rapidly leads to a mixture of *cis*- and *trans*-stilbene, 11 per cent *cis*, very close to that reported³¹ as the photostationary state under similar conditions. The stereospecificity of the photoelimination indicates a concerted process in this case; however, results with the unsymmetrical azasuccinic anhydrides (*Figure 14*) show that photoeliminations from 1,2-dicarboxylic anhydrides need not be concerted.

In these unsymmetrically substituted anhydrides²⁸, with separated chromophores, the photolytic elimination path is dependent on which chromophore

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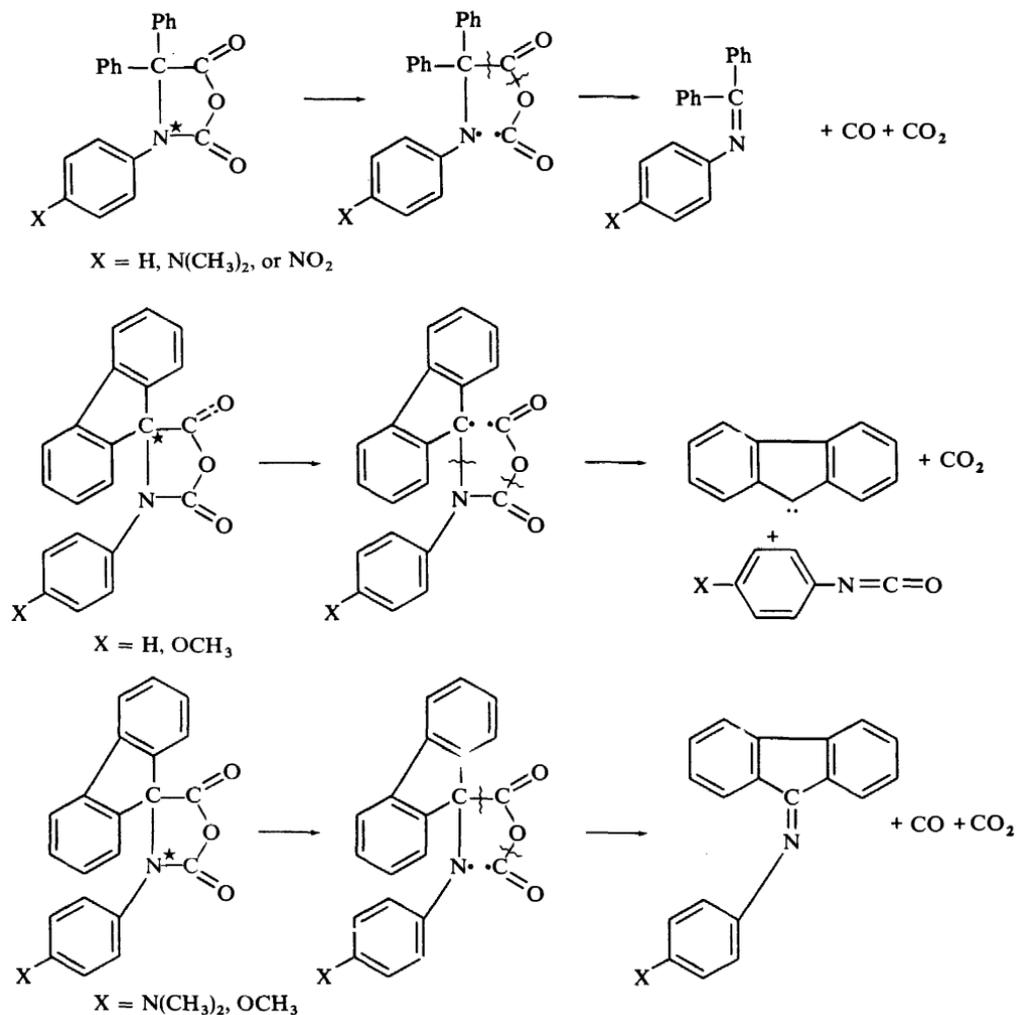


Figure 14. Substituent effect on photolysis of triarylazasuccinic anhydrides

has the lowest excited singlet state. When this is the azaanhydride function, as shown by the position of the star in Figure 14, the expected elimination of carbon dioxide and carbon monoxide occurs, while if the aryl substituents bound to the tetrahedrally substituted anhydride ring carbon have the lowest excitation energy, cleavage takes place in a different manner yielding a carbene, an isocyanate and carbon dioxide. Where there is a borderline situation as in the *p*-anisyl derivative, both photoreactions proceed simultaneously. Although these reactions are not photofluorescent processes, they illustrate that there is no simple, overwhelmingly dominant pathway in the photodecomposition of dicarboxylic anhydrides.

While there had been precedents in examples of photoelimination from 1,2-dicarboxylic anhydrides, one could not be certain of what to expect on

attempting photolysis of a 1,4-cyclohexadiene-3,6-dicarboxylic anhydride. Although the photolysis of these anhydrides had not been previously examined, they had interesting possibilities as photofluorescers. The compound we considered first in this regard was the 9,10-dicarboxy anhydride of 9,10-diphenyl-9,10-dihydroanthracene shown in *Figure 15*. This 1,4-bridged

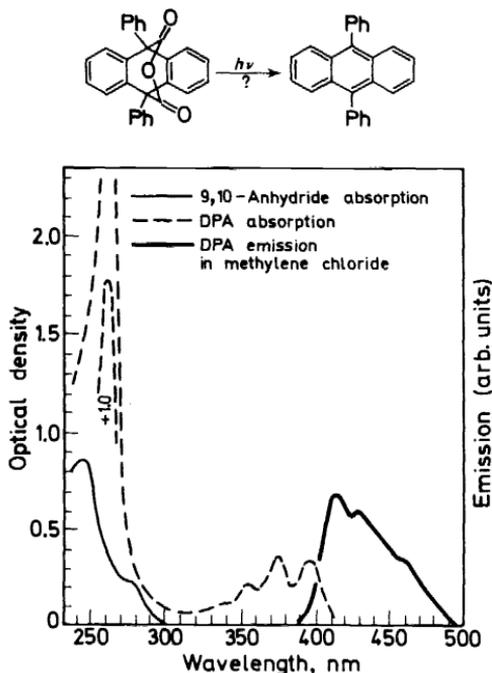


Figure 15

anhydride only has isolate benzene and carboxyanhydride chromophores and thus absorbs only at short wavelengths—below 290 nm. If it photoeliminates carbon monoxide and carbon dioxide it would give 9,10-diphenylanthracene (DPA), a very efficient blue emitting fluorescer that absorbs strongly out to 400 nm. The DPA photoproduct also absorbs strongly at the short wavelengths needed to produce it. Although this will be a drawback in some situations under conditions where low percentage conversion can be used it may not be a serious disadvantage. The question that was therefore initially of greatest concern was simply whether or not the photochemistry would proceed.

Quite fortunately this thermally stable (m.pt > 245°) anhydride had recently been prepared for the first time³² and a small sample was available. An initial experiment showed that the quantum yield of photoelimination to produce 9,10-diphenylanthracene in methylene chloride was about 50 per cent and no side reactions could be detected.

The generality of the efficient photoelimination of carbon monoxide and carbon dioxide from 9,10-dihydroanthracene-9,10-dicarboxyanhydrides was established by photolysing the known³³ 9,10-dihydrogen and 9,10-analogues as shown in *Figure 16*. The efficiencies of conversion on direct

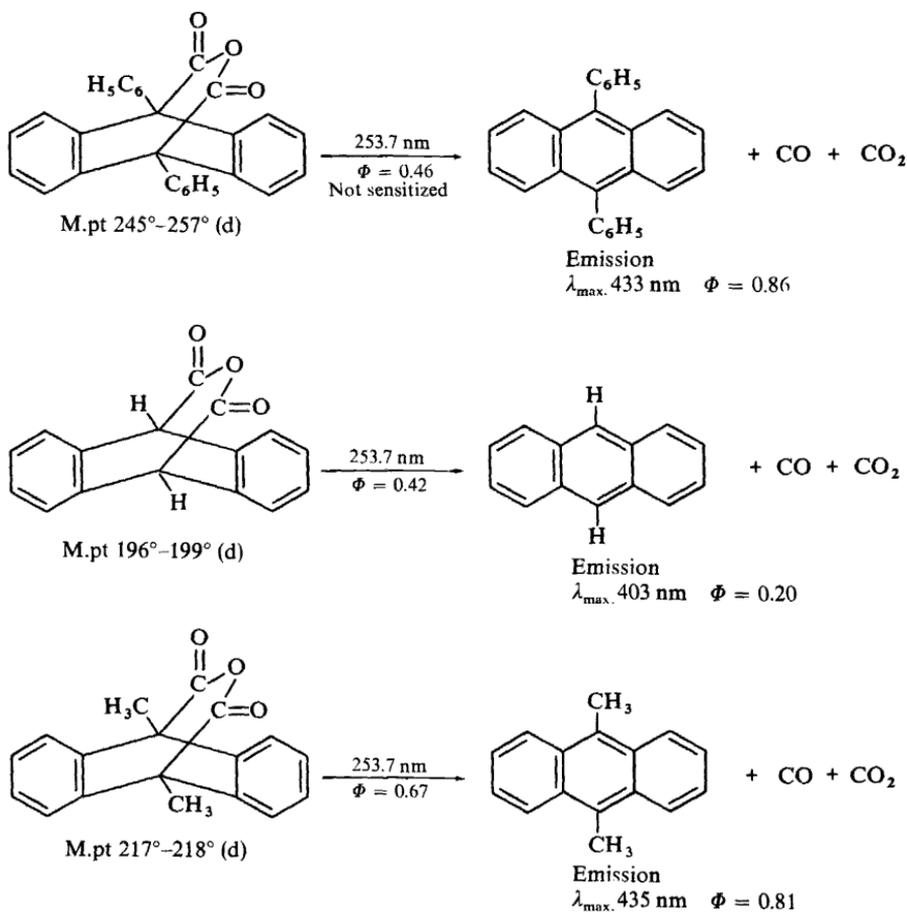


Figure 16. Photolysis of 9,10-dihydroanthracene-9,10-dicarboxylic anhydrides

excitation with 253.7 nm radiation are all high. The photolysis to produce anthracenes could not be sensitized by acetone, acetophenone or even benzene. All three of these anhydrides are thermally stable to the melting point ranges indicated in Figure 16 where decomposition begins to occur. This is a significant advantage over other, much more thermally labile photoprecursors of anthracenes.

Unexpected difficulties were encountered in repeating the preparation of 9,10-diphenyl-9,10-dihydroanthracene-9,10-dicarboxylic anhydride through the conventional procedure of alkali metal reduction, carboxylation and dehydration with acetic anhydride. This was traced to the conformational preference shown in Figure 17 for the intermediate 9,10-diphenyl-9,10-dihydroanthracene, 9,10-dicarboxylic acid to exist with the phenyl groups occupying the less hindered axial positions. In this conformation phenyl interference with the *o*-hydrogens of the benzo rings does not occur, leaving the smaller carboxylic acid functions in the equatorial positions where they cannot participate in intramolecular dehydration. With employment of

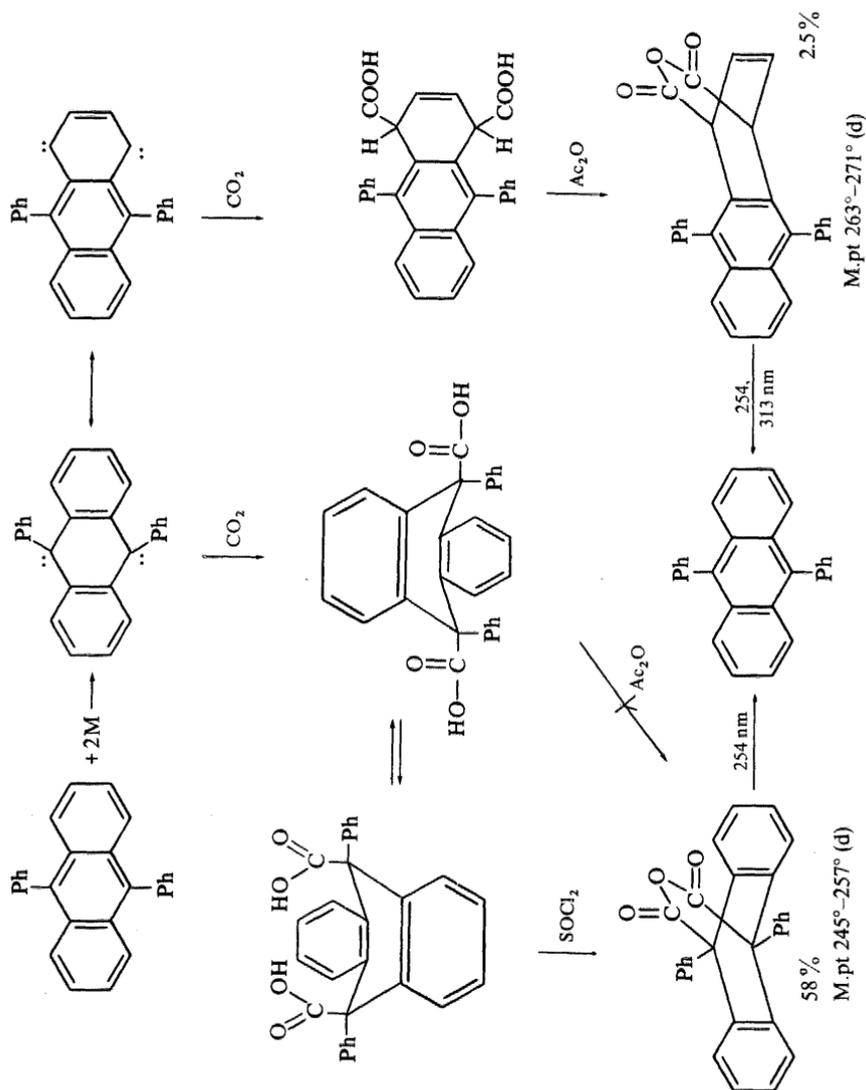


Figure 17. Synthesis of 9,10-diphenylanthracene dihydrodicarboxylic anhydrides

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thionyl chloride as a dehydrating reagent this problem could be circumvented and the desired intramolecular anhydride could be prepared in good yield³⁴. We presume that an intermediate is formed which inverts the boat conformation of the 1,4-cyclohexadiene ring, returning the carboxylic acid functions to the axial positions required for cyclization. In finding conditions suitable for synthesis of this 9,10-dicarboxylic anhydride we also isolated and characterized a small yield of the isomeric 1,4-anhydride; 9,10-diphenyl-1,4-dihydroanthracene; 1,4-dicarboxylic anhydride³⁴. This material also proved to undergo photoelimination efficiently and proved useful as a photo-fluorescer.

The spectroscopic changes that occur on direct photolysis of 9,10-diphenyl-1,4-dihydroanthracene-1,4-dicarboxylic anhydride are shown in Figure 18. The photoelimination proceeds with high quantum efficiency

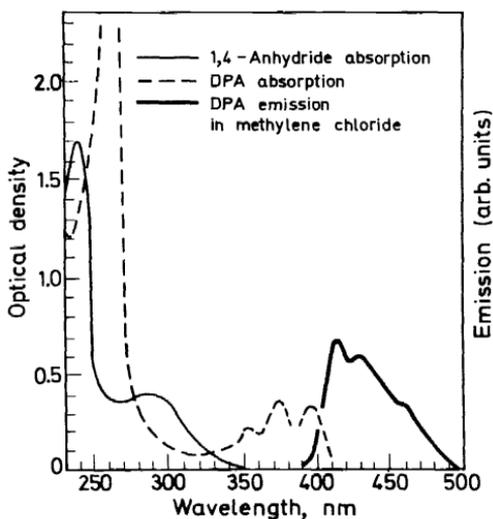
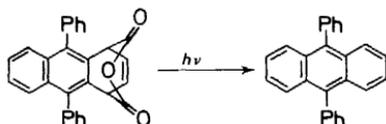


Figure 18

($\Phi = 0.67$) in methylene chloride solution and could not be sensitized with acetone or benzene. Despite the presence of the normally fluorescent 1,4-diphenylanthracene chromophore³⁵, this anhydride exhibited very little room temperature fluorescence. A notable characteristic of this system, quite different from the 9,10-anhydrides, is its typical naphthalenic absorption in the 300 nm region where absorption by the 9,10-diphenylanthracene product is at a minimum. This permits efficient photolysis to high levels of conversion and also proves invaluable for the experimental

determination of whether the product is formed in an excited state, the fundamental question referred to at the beginning of this talk.

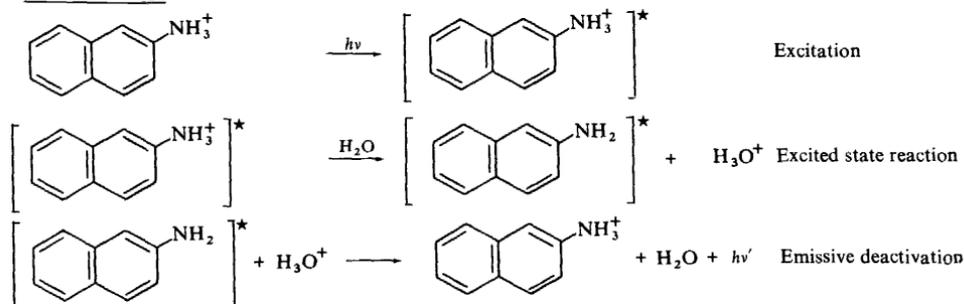
There are numerous examples in the literature (*Figure 19*) where products have been shown to be photolytically produced in emitting excited states. In these cases the excited products are either protolysis products³⁶ or excimers³⁷ or exciplexes³⁸ which do not have a stable ground state under the emitting conditions. Indeed, the experimental evidence for all these known examples being produced in the excited state is most convincing *because* the photoproduct has no stable ground state under the photolysis conditions and therefore the emission cannot be due to the trivial two-quantum process of ground state product formation and subsequent excitation. When a stable fluorescent product is formed, the experimental problem of how to differentiate between the direct single-quantum conversion to an excited product and the two-quantum conversion to the same excited product arises. Fortunately, if excitation of the precursor can be achieved efficiently with wavelengths not strongly absorbed by the product, a relatively simple means can be devised to distinguish between the two. As indicated earlier, these conditions are met in the photoconversion of 9,10-diphenyl-1,4-dihydroanthracene-1,4-dicarboxylic anhydride to 9,10-diphenylanthracene (DPA) by wavelengths near 300 nm. At 313 nm, where an easily isolated mercury line emits, the ratio of extinction coefficients of anhydride and DPA is about 6:1. With this wavelength, if DPA is initially generated in its emitting excited state as in Case I in *Figure 20* with a square wave steady state light source, one should see an initial relatively strong emission flux which decreases in intensity as the concentration of precursor decreases as the reaction proceeds. Conversely, if the product DPA is generated in its ground state and is only subsequently available for excitation, then as seen in Case II of *Figure 20* the initial change in emission flux is inversely proportional to the change in concentration of the precursor and the emission will grow as the reaction proceeds.

An initial set of experiments was made with a 313 nm radiation source causing the photoconversion of a 10^{-4} M solution of the 1,4-anhydride in methylene chloride solution in a 1.5 mm diameter tube. Under these conditions with a small volume ($\sim 8 \times 10^{-3}$ ml) of undegassed solution, emission in the 430–460 nm region was continuously detected and recorded. As shown in *Figure 21*, there was no detectable deviation in the steady development of DPA fluorescence (above background) from that predicted from the Case II kinetic expression. From this study, which was carried out to high percentage (>95 per cent) conversion, and comparison with emission from known concentrations of DPA in similar tubes, we estimate that less than 0.1 per cent (one part in a thousand) of the emitting DPA could have been photoproducted directly from the 1,4-anhydride. Furthermore, the close agreement of observed kinetic behaviour for the entire (>95 per cent) reaction with predicted Case II behaviour demonstrates that the anhydride is not a quencher for DPA emission at these concentrations.

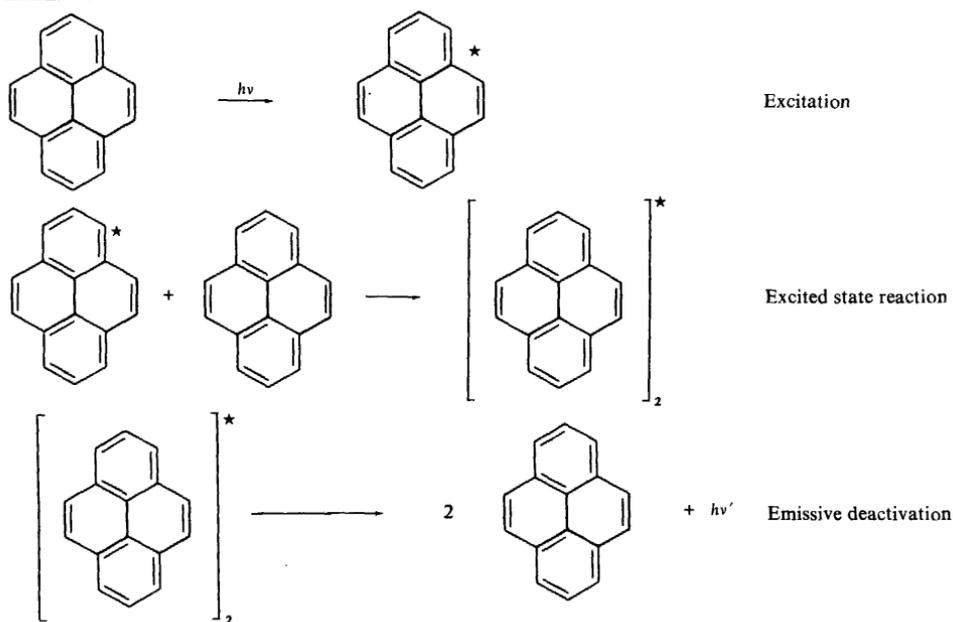
In order to improve the detectability of possible photogenerated emitting states in this system, we changed to an experimental configuration allowing better reproducibility in measurement of relative emission signals from sample to sample during the initial stage of photogenerated reaction. This configuration involved a total sample volume much larger than the illuminated volume,

PHOTOCHEMICAL GENERATION OF STABLE FLUORESCENT COMPOUNDS

PROTOLYTIC:



EXCIMER:



EXCIPLEX:

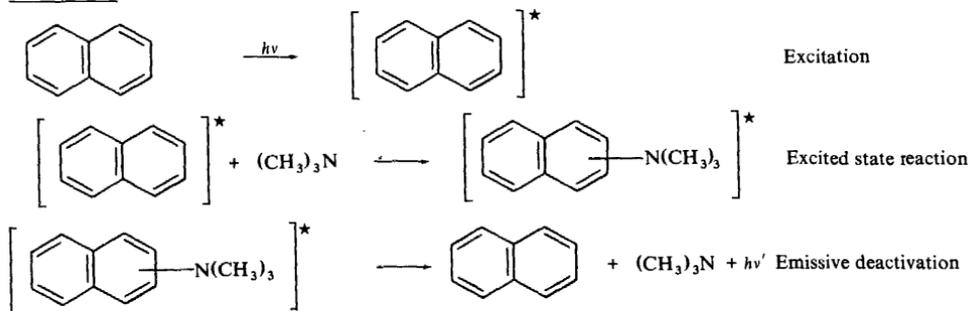
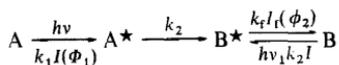


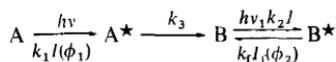
Figure 19. Emission from species photolytically generated in their excited states

Case I: Photogenerated excited state



$$dI_f/dt \approx \phi_1 \phi_2 I K_1 dA/dt$$

Case II: Secondary excitation of photogenerated ground state



$$dI_f/dt \approx -\phi_2 I K_2 dA/dt$$

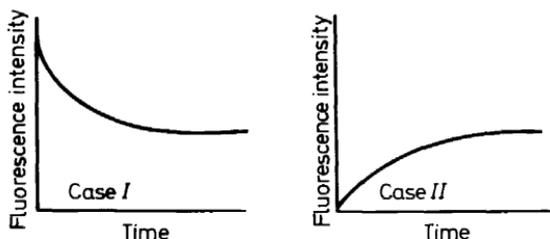


Figure 20. Nature of photogenerated state of stable fluorescer

with observation of luminescence limited to a fraction of the front portion of the illuminated volume. Detection sensitivity was adjusted to give a reliable signal for residual luminescence from the solvent as a baseline, when excitation intensity was adjusted to give less than 0.1 per cent reaction in one second. Irradiation was started by manual removal of a shutter, which required less than 20 milliseconds. In Figure 22 we show a typical oscilloscope trace of the emission signal during the first 400 milliseconds of exposure of the solution. The signal at the time shutter removal is complete is tabulated below the trace for several independent experiments using a 5×10^{-4} M solution of 1,4-anhydride, along with comparable data for solvent from the same source (arrows indicate sequence of measurements). No initial signal above the blank is observed, within the error of measurement. This error is estimated

DPA emission (420-460 nm)/time of irradiation
(313 nm) of 1,4-anhydride (10^{-4} M in CH_2Cl_2)

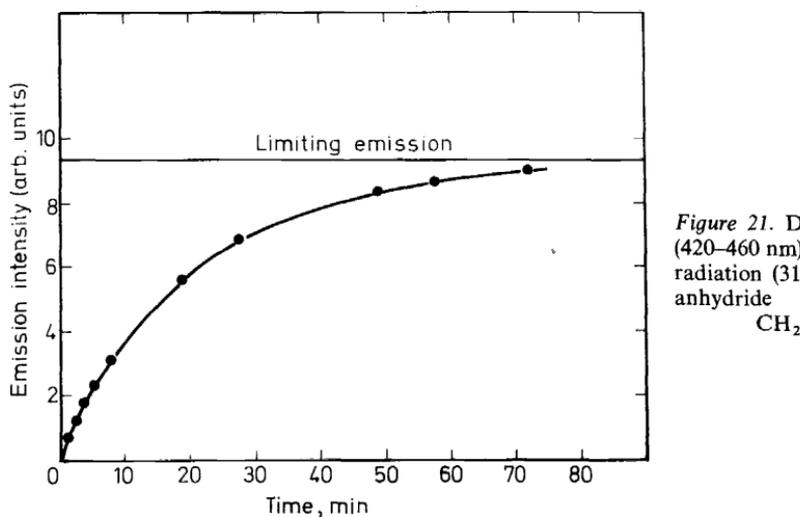


Figure 21. DPA emission (420-460 nm) time of irradiation (313 nm) of 1,4-anhydride (10^{-4} M in CH_2Cl_2)

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to be less than 1.5 units in the arbitrary scale indicated. For comparison purposes, the signal from a 10^{-3} M DPA solution (which is about one third as efficient in absorbing radiation at this wavelength) is over 9000 units in this experimental configuration. Since the quantum efficiency for conversion of the anhydride is 67 per cent, and the quantum efficiency of DPA emission is ~ 90 per cent, under these conditions we conclude that if any excited DPA is produced directly from the excited anhydride, the amount so produced must be less than 0.01 per cent.

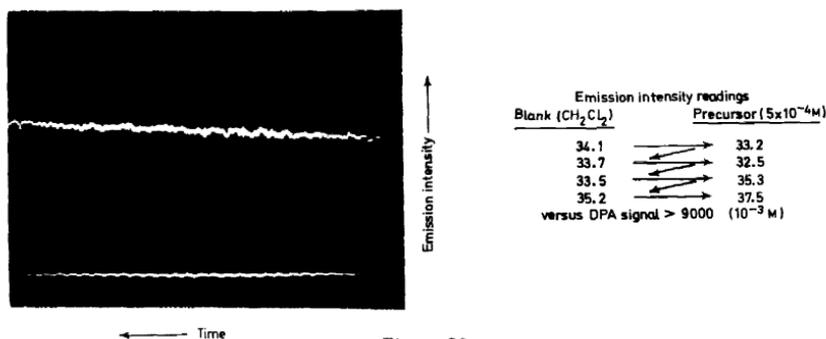


Figure 22

The study of stable photofluorescers is a fruitful way of gleaning information about excited state transformations. We can reasonably expect that as more systems are studied, new classes of products generated in excited states will emerge and a better understanding of the potential energy surfaces of photochemical reactions will be obtained.

ACKNOWLEDGEMENT

Thanks are due to many colleagues at the American Cyanamid Company. Special mention should be given to Dr K. R. Huffman for synthesis of photofluorescers, Dr F. Halverson for helpful discussion of the kinetics and for designing and conducting the search for excited state fluorescer generation and Dr G. W. Kennerly for his encouragement and support of photofluorescer research.

REFERENCES

- 1 Th. Förster, *Pure Appl. Chem.* **24**, 443 (1970);
(a) J. Menter and Th. Förster, *Photochem. Photobiol.* **15**, 289 (1972).
- 2 C. A. Parker, *Photoluminescence of Solutions*, p 398. Elsevier: Amsterdam (1968).
- 3 A. Zweig, Symposium III. *Unconventional Photographic Systems*, 20-23 October 1971, SPSE Abstracts p 79.
- 4 G. R. Bird, Symposium III. *Unconventional Photographic Systems*, 20-23 October 1971, SPSE Abstracts p 4.
- 5 G. N. Lewis, T. T. Magel and D. Lipkin, *J. Amer. Chem. Soc.* **62**, 2973 (1940).
- 6 D. Schulte-Frohlinde, *Liebigs Ann.* **615**, 114 (1958);
D. Schulte-Frohlinde, H. Blume and H. Gusten, *J. Phys. Chem.* **66**, 2486 (1962);
D. Gegiou, K. A. Muszkat and E. Fischer, *J. Amer. Chem. Soc.* **90**, 3907 (1968).

- ⁷ D. A. Rogers, J. D. Margerum and G. M. Wyman, *J. Amer. Chem. Soc.* **79**, 2464 (1957); J. Blanc and D. L. Ross, *J. Phys. Chem.* **72**, 2817 (1968).
- ⁸ E. Lippert and W. Luder, *J. Phys. Chem.* **66**, 2430 (1962); F. Feigl, H. E. Feigl and O. Goldstein, *J. Amer. Chem. Soc.* **77**, 4162 (1955); B. N. Mattoo, *Trans. Faraday Soc.* **52**, 1184 (1956); **53**, 760 (1957); P. Schwarze and R. Hoffschmidt, *Naturwissenschaften*, **46**, 205 (1959); C. E. Wheelock, *J. Amer. Chem. Soc.* **81**, 1348 (1959).
- ⁹ E. H. White, C. W. Friend Jr, R. L. Stein and H. Maskill, *J. Amer. Chem. Soc.* **91**, 523 (1969). (a) S. Sharafy and K. A. Muszkat, *J. Amer. Chem. Soc.* **93**, 4119 (1971).
- ¹⁰ C. S. Wood and F. B. Mallory, *J. Org. Chem.* **29**, 3373 (1964); R. F. Evans, *J. Chem. Educ.* **48**, 768 (1971).
- ¹¹ K. S. Wei and R. Livingston, *Photochem. Photobiol.* **6**, 229 (1967).
- ¹² G. Loefer, *Chem. Abstr.* **64**, 12495 (1966); I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, p 21 (1965).
- ¹³ D. Bellus, *Advanc. Photochem.* **8**, 109 (1971).
- ¹⁴ O. Buchardt, *Tetrahedron Letters*, 1911 (1968).
- ¹⁵ K. Uchida, *Bull. Chem. Soc., Japan*, **36**, 1097 (1963) and references therein; R. G. Brault and J. D. Margerum, Abstr. 155th ACS meeting, San Francisco (1968).
- ¹⁶ G. Pfundt and S. Farid, *Tetrahedron*, **22**, 2237 (1966).
- ¹⁷ R. L. Letsinger and R. R. Hautala, *Tetrahedron Letters*, 4205 (1969).
- ¹⁸ J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.* **86**, 5277 (1964); J. C. Sheehan, R. M. Wilson and A. W. Oxford, *J. Amer. Chem. Soc.* **93**, 7222 (1971).
- ¹⁹ K. R. Huffman, C. E. Kuhn and A. Zweig, *J. Amer. Chem. Soc.* **92**, 599 (1970).
- ²⁰ Unpublished study with Dr J. B. Gallivan.
- ²¹ E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.* **88**, 1844 (1966); B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.* **89**, 6911 (1967).
- ²² A comprehensive review of fluorescent materials suitable for use as scintillators can be found in R. C. Sangster and J. W. Irvine Jr, *J. Chem. Phys.* **24**, 670 (1956).
- ²³ B. Singh, A. Zweig and J. B. Gallivan, *J. Amer. Chem. Soc.* **94**, 1199 (1972).
- ²⁴ W. A. Henderson Jr and A. Zweig, *J. Amer. Chem. Soc.* **89**, 6778 (1967); W. A. Henderson Jr, R. Lopresti and A. Zweig, *J. Amer. Chem. Soc.* **91**, 6049 (1969).
- ²⁵ (a) H. Prinzbach, R. Kitzing, E. Druckey and H. Achenbuch, *Tetrahedron Letters*, 4265 (1966); (b) P. Courtot and R. Rumin, *Tetrahedron Letters*, 1091 (1968); (c) R. Kitzing and H. Prinzbach, *Helv. Chim. Acta*, **53**, 158 (1970).
- ²⁶ J. S. Krull and D. R. Arnold, *Tetrahedron Letters*, 4349 (1969).
- ²⁷ K. R. Huffman and A. Zweig, to be published.
- ²⁸ W. A. Henderson Jr and A. Zweig, *Tetrahedron*, **27**, 5307 (1971).
- ²⁹ W. A. Henderson Jr and A. Zweig, *J. Chem. Soc. (D)*, 169 (1972).
- ³⁰ J. B. Birks, *Photophysics of Aromatic Molecules*, p 184. Wiley-Interscience: London (1970).
- ³¹ G. Zimmerman, L. Chow and U. Paik, *J. Amer. Chem. Soc.* **80**, 3528 (1958).
- ³² M. M. Rauhut, D. Sheehan, R. A. Clarke and A. M. Semsel, *Photochem. Photobiol.* **4**, 1097 (1965).
- ³³ A. H. Beckett and B. A. Mulley, *J. Chem. Soc.* 4159 (1955), and references therein.
- ³⁴ K. R. Huffman and A. Zweig, to be published.
- ³⁵ A. Zweig and J. B. Gallivan, *J. Amer. Chem. Soc.* **91**, 260 (1969).
- ³⁶ A. Weller, *Progress in Reaction Kinetics*, **1**, 187 (1961).
- ³⁷ T. Förster, *Angew. Chem. Internat. Edit.* **8**, 333 (1969).
- ³⁸ A. Weller, *Pure Appl. Chem.* **16**, 115 (1968).