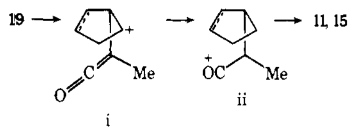
(59) Other effects which might control the stereochemistry of cyclopropyl ester have been considered as follows. (a) For two-step ionization–ring contraction, **19** may prefer decomposition to the more stable epimer of **20**, in which the larger group (methyl) is exo.[60] A subtle version of this effect, considering a *stepwise* ring contraction, reflects the most likely preferred conformation for ketene cation (i) leading to endo acylium ion (ii).



(b) Concerted rearrangement of excited ketones might give acid chlorides (which are trapped by methanol) via four-center ring contraction–chlorine migration. However, conformations with equatorial chlorine are best arranged for this process, and the products predicted for decomposition of **5, 7e'** (analogous to **23**) would be inconsistent with our pattern of results. (c) We thank Professor R. G. Bergman for helpful discussions concerning these points.

(60) Epimerization studies carried out on 6-carbomethoxybicyclo[3.1.0]hex-2-ene indicate a preference for exo substitution by the larger group; see D. L. Garin and D. J. Cooke, *J. Chem. Soc., Chem. Commun.*, 33 (1972).

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(62) (a) G. Roussi and R. G. Beugelmàns, *Tetrahedron Lett.*, 1333 (1972); (b) P. Yates and R. Hagens, *ibid.*, 3623 (1969).

(63) F. Arndt in "Organic Syntheses", Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N.Y., 1943, p 165.

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Excited-State Multiplicity for the Direct Photochemical Isomerization of Azomethine Dyes

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Abstract: Azomethine dyes are known to isomerize readily about the C═N bond following photochemical excitation in fluid solution at ambient temperatures. This excitation of the dyes can be brought about either directly by absorption of light or indirectly by energy transfer from an appropriate triplet sensitizer. To determine whether the isomerization following direct excitation occurs in the singlet or triplet manifolds, the effects of oxygen as well as external and internal heavy atoms on the isomerization of selected benzoylacetanilide and pyrazolone azomethine dyes were examined. In the absence of any heavy atoms, deaerated and air-saturated solutions produce the same quantities of transient species following flash excitation. The presence of either solvent heavy atoms or appropriately substituted intramolecular heavy atoms increases the quantity of transient species produced and, furthermore, part of the transient species formation can be quenched when oxygen is dissolved in the experimental solutions. The conclusion is that in the absence of any heavy atoms, isomerization proceeds via the lowest excited-singlet state of the dyes, but with internal or external heavy atoms present, triplet isomerization, partially quenchable by dissolved oxygen, makes a contribution. By assuming diffusion-controlled quenching of dye triplets by molecular oxygen, one can estimate the triplet-state lifetime of a pyrazolone azomethine dye with an intramolecular heavy atom to be 10 ns.

Azomethine dyes are known to undergo geometric isomerization about the carbon–nitrogen double bond following excitation with light.[1,2] If flash photolysis techniques are employed, dye isomerization can be readily observed through changes in the dye absorption spectra following flash excitation. In fluid solution at ambient temperatures, the photochemical isomerization to the less-stable dye isomers is only temporary and followed by thermal relaxation to regenerate the more stable isomers. Both direct excitation with light and indirect excitation by energy transfer from appropriate triplet-state photosensitizers are effective in bringing about dye isomerization. The results show that the photosensitizers lead to excitation of the lowest excited triplet states in the dyes and demonstrate that the dyes can isomerize in this state. Until now, however, there has been no evidence to distinguish between singlet- and triplet-state isomerization when the dyes are excited directly.

The two possible excited electronic states for isomerization about essential double bonds are the lowest excited singlet and triplet states. For each case there are known examples. Stilbene, one of the most extensively investigated systems insofar as isomerization is concerned, isomerizes in the singlet manifold following absorption of light.[3,4] Singlet isomerization also obtains with the *O*-methyloxime ethers of acetophenone[5] and the 4-nitrophenylhydrazones of benzaldehyde.[6] Compounds shown to isomerize in their lowest excited triplet states include 3,3′-diethyl-9-methylthiacarbocyanine,[7] thioindigo,[8] 6,6′-diethoxythioindigo,[8] and *trans*-1-phenyl-2-(2-naphthyl)ethylene.[9]

On the basis of past results, we knew of no way to predict reliably a singlet- or triplet-state isomerization path in azomethine dyes and found it necessary to devise experiments to make this distinction. These experiments are based upon two well-known phenomena in photochemistry. The first of these is quenching of excited electronic states. Ideally, one tries to employ a quencher that, by virtue of the position of its energy levels, quenches exclusively the triplet state by energy transfer. Even if one must settle for a quencher that has the potential for quenching both singlets and triplets, quenching experiments will usually accomplish their purpose because lowest excited triplet states are, in most cases, substantially longer-lived and thus more easily quenched than their singlet-state counterparts. Because of the very low triplet-state energies in azomethine dyes,[10,11] we were severely limited in our choice of quenchers. The one quencher that met our requirements was molecular oxygen. Although the lowest triplet states of many of the azomethine dyes actually are lower in energy than the lowest singlet state of oxygen,[10,11] the lowest excited electronic state in this molecule, oxygen still has the potential for quenching such dye triplet states by catalyzing intersystem crossing from the dye triplet to the dye ground state. We consider two possible quenching reactions involving dye triplet states and molecular oxygen as shown in the equations

$$^3D^* + {}^3O_2 \rightarrow {}^1D + {}^1O_2^* \tag{1}$$

$$^3D^* + {}^3O_2 \rightleftharpoons {}^3({}^3D^3O_2)^* \rightarrow {}^1D + {}^3O_2 \tag{2}$$

where D represents an azomethine dye, the superscripts denote

Table I. Initial Changes in Absorbance[a,b] Following Flash Excitation of Dyes I and II in Benzene

	Flash discharge energy, J		
Solutes[c,d]	100	156	225
Dye I	0.218 ± 0.003	0.336 ± 0.006	0.461 ± 0.004
Dye I, air	0.218 ± 0.002	0.335 ± 0.005	0.457 ± 0.004
Dye I, benzanthrone	0.298 ± 0.003	0.451 ± 0.004	0.608 ± 0.003
Dye I, benzanthrone, air	0.220 ± 0.002	0.332 ± 0.002	0.452 ± 0.005
Dye II	0.135 ± 0.002	0.202 ± 0.002	0.272 ± 0.002
Dye II, air	0.132 ± 0.002	0.203 ± 0.003	0.268 ± 0.003
Dye II, oxygen	0.134 ± 0.003	0.199 ± 0.004	0.272 ± 0.002
Dye II, benzanthrone	0.197 ± 0.002	0.287 ± 0.003	0.376 ± 0.003
Dye II, benzanthrone, air	0.130 ± 0.002	0.199 ± 0.002	0.265 ± 0.003

[a] The changes in absorbance were measured at 520 nm for dye I and 630 nm for dye II. [b] Each entry is the average of five to seven measurements. [c] The concentration of each dye solution was 2 × 10^{-5} M. [d] When employed, the concentration of benzanthrone was 2 × 10^{-5} M.

the multiplicity of the electronic states, and the asterisks signify excited states.[12-15] Reactions 1 and 2, even at maximum efficiency, are limited by spin statistical factors of one-ninth and one-third, respectively. Moreover, as the energy of the donor triplet state approaches that of singlet oxygen, the rate of the reverse of reaction 2 approaches that of the forward reaction and leads to an additional reduction in quenching rate.[15] It is fair to state that the maximum possible quenching rate of dye triplets by molecular oxygen will be near one-half that of a diffusion-controlled reaction and, in practice, the actual rate probably will be somewhat less.

Molecular oxygen also has the potential for quenching the lowest excited singlet states of our dyes. Kearns lists three important, energetically feasible reactions for oxygen quenching of excited singlet-state molecules; these reactions in terms of dye singlet states are shown in the equations[13]

$$^{1}D_1{}^* + {}^{3}O_2 \rightarrow D^+ + O_2^- \qquad (3)$$

$$\rightarrow {}^{3}D_2{}^* + {}^{3}O_2{}^* \qquad (4)$$

$$\rightarrow {}^{3}D_1{}^* + {}^{3}O_2{}^* \qquad (5)$$

The subscripts 1 and 2 for D indicate first and second excited states, respectively. According to Kearns, relaxation to the charge-transfer state is expected to be the dominant mechanism by which oxygen quenches excited singlet-state molecules whenever the charge-transfer state lies below the first excited singlet state of the dye; if the charge-transfer state is higher in energy, reactions 4 and 5 should provide the principal paths for singlet deactivation.[13] Singlet-state quenching by molecular oxygen should proceed at the diffusion-controlled rate.[13,15]

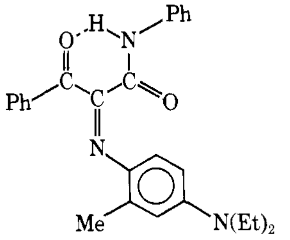
Although molecular oxygen is a powerful quencher of both excited singlet and triplet states, the oxygen quenching effect will be negligible unless the excited states to be quenched have lifetimes sufficiently long to be intercepted. It is known from our inability to observe any excited-state absorption in azomethine dyes following flash excitation that both the lowest excited singlet and triplet states in azomethine dyes are shorter lived than 10^{-5} s, the time resolution limit of our flash apparatus.[1,10] For oxygen-quenching experiments to be useful in distinguishing between singlet- and triplet-state isomerization paths for azomethine dyes, the dye triplets must simultaneously be substantially longer-lived than the dye singlets and sufficiently long-lived to be intercepted by molecular oxygen. The required limits for dye triplet lifetimes under our experimental conditions are given below.

The second photochemical phenomenon to be applied in these experiments is the heavy-atom effect. Since the first reports by McClure[16] and Kasha,[17] it has been known that heavy atoms have important effects on processes involving triplet states of organic molecules. Heavy atoms either intramolecularly or intermolecularly increase spin-orbit coupling between the singlet and triplet manifolds and thus facilitate intersystem crossing between the two. The manifestations of the presence of heavy atoms are shorter lifetimes for both singlet and triplet states, increased yields of triplet states, and increased intensity for absorption from the ground state to the triplet manifold. It was the property of increased yields of triplet states that we hoped to apply in these experiments.

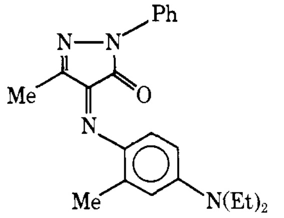
It was our purpose in a series of experiments to employ both heavy-atom and oxygen quenching effects to try to resolve the question of whether the isomerization of azomethine dyes proceeds through the lowest excited singlet or triplet states. We wanted to see whether the formation of the dye isomers could be quenched with molecular oxygen and also wanted to investigate the effects of inter- and intramolecular heavy atoms on both the quantity and the quenchability of dye isomer formation.

Results and Discussion

Two azomethine dyes, a benzoylacetanilide (I) and a pyrazolone (II), were selected for initial experimental investigations. The illustrated syn configurations are more stable for both I[18] and II.[19-21] The absorption maxima of the less-stable anti isomers in both cases are at wavelengths longer than the syn isomer maxima. Given elsewhere are the absorption spectra for both the more-stable and less-stable dye isomers.[1,19,22,23]



I



II

For dyes I and II, monitoring wavelengths were selected where substantial increases in absorption occurred following flash excitation of each of the dyes in benzene at room temperature. Since the gains in absorbance from syn-anti isomerization are only temporary and followed by thermal regeneration of the starting dye isomers, the initial changes in absorbance were measured. To see whether or not these conversions to the less-stable isomers were quenchable by oxygen, these measurements were carried out both in degassed and air-saturated dye solutions; for dye II, the experimental solution also was saturated with pure oxygen in place of air. The presence of oxygen in the dye solutions had no effect on the quantity of dye isomer formed. In the presence of benzan-

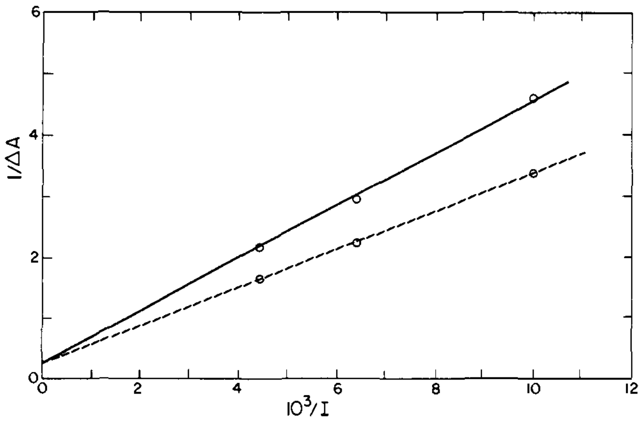


Figure 1. Plots of $1/\Delta A$ vs. $1/I$ for dye I in benzene solution. The solid line corresponds to a degassed solution without sensitizer and the dashed line to a degassed solution with sensitizer.

throne, a triplet sensitizer, substantially more transient was produced for both dyes so long as the solutions were degassed, but upon admission of air to these solutions, the quantity of transient was reduced to a level of slightly less than or equal to that in the absence of benzanthrone. It appears that the oxygen in air-saturated solutions quenches the sensitizer triplets before any energy can be transferred to the dyes. The possible small reduction in the quantity of dye isomer produced can be attributed to competitive absorption between the dye and the sensitizer. Results are summarized in Table I. As determined from measurements of solution absorption spectra before and after the flash photolysis experiments, there was no evidence for any permanent reaction of the dyes in competition with the isomerization and energy-transfer reactions.

All measuremets of changes in dye absorbance were carried out at three different flash discharge energies. The flash intensities are proportional to the discharge energies over the range used in these experiments. Using the method of McClure[24,25] and plotting $1/\Delta A$ vs. $1/I$, where ΔA is the observed change in absorbance and I is the relative flash intensity, one obtains straight lines as shown for dyes I and II in Figures 1 and 2, respectively. Extrapolation to infinite light intensity leads to approximately the same values for the limiting change in absorbance both in the presence and absence of sensitizer. These extrapolated changes in absorbance would correspond to the absorbance change observed if the photostationary state composition of dye isomers were reached following absorption of a large quantity of light. If markedly different extrapolated changes in absorbance had been obtained both in the absence and presence of sensitizer, one could invoke the involvement of different excited states, the singlet state in the former case and the triplet state in the latter case. When the extrapolated differences in absorbance are either small or zero, no conclusions about the excited state responsible for the isomerization are possible, because it is possible that the isomerization efficiencies in the singlet and triplet states may be identical or nearly so and also allowances must be made for a certain amount of experimental error. Results up to this point show only that the state responsible for isomerization of the dyes upon direct irradiation is too short-lived so be intercepted by oxygen dissolved in benzene.

Next investigated was the effect of external heavy atoms on the quantity of dye transient produced following flash excitation. The solvents employed here were chlorobenzene, bromobenzene, and iodobenzene. Relative to benzene, the absorption spectra of dyes I and II shift somewhat to longer wavelengths in these solvents. For this reason, the wavelengths selected for monitoring the conversions to the less-stable isomers were also shifted by like amounts to longer wavelengths.

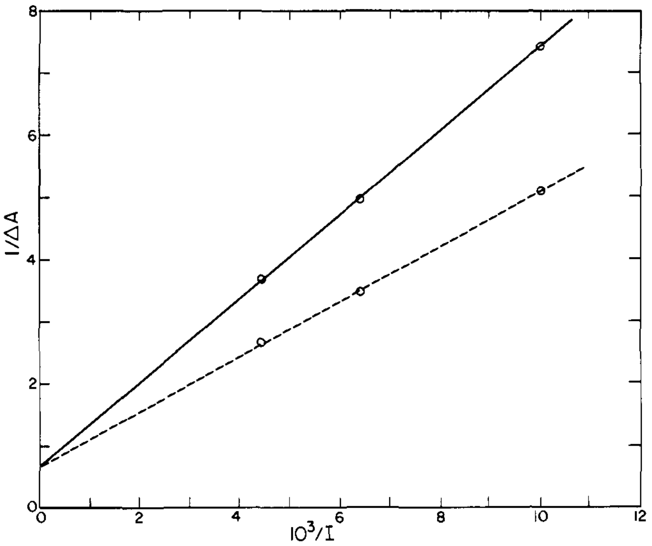


Figure 2. Plots of $1/\Delta A$ vs. $1/I$ for dye II in benzene solution. The solid line corresponds to a degassed solution without sensitizer and the dashed line to a degassed solution with sensitizer.

Table II summarizes the results that show that the observed changes in absorbance following flash excitation of dyes I and II are all larger in the heavy-atom solvents than in benzene. One can rationalize these larger ΔA's in terms of heavy-atom-induced intersystem crossing to the triplet manifold, resulting in a greater contribution to the isomerization quantum yield from the triplet route. By itself, this is not a strong argument, because we have not shown that the absorption spectra of the less-stable dye isomers show the same solvent shifts in their absorption spectra as do the more stable isomers. There is, however, additional evidence that in benzene no dye triplets are formed upon photoexcitation, but that the halogenated solvents do effect some intersystem crossing to the dye triplet manifold. In contrast to previous observations in benzene, the quantity of dye isomer observed following flash excitation of the heavy-atom solutions of dyes is smaller in air-saturated solution than in degassed solution. In benzene there was no difference, within experimental error, of the quantity of dye isomer generated in the presence and the absence of dissolved oxygen. In the heavy-atom solvents, however, the differences under the two conditions, although small, are, in many cases, outside the range of experimental error and we believe the effect to be real. These data, all listed in Table II, show that oxygen in heavy-atom solvents is effective in quenching a small portion of the excited states preceding the formation of the dye isomers. Since oxygen does not have the same effect in benzene solution, the logical conclusion is that no dye triplets are produced upon direct irradiation of the dyes in benzene and the isomerization in this solvent is exclusively a singlet-state isomerization; the heavy-atom solvents effect at least partial conversion from the singlet to the triplet manifolds in the dyes and the triplet states can be at least partially intercepted and quenched by dissolved oxygen. Since heavy atoms tend to shorten the lifetimes of both the lowest excited singlet and triplet states, the quenching of dye triplets must be less effective in the halogenated solvents than it would be in benzene if dye triplets were formed directly in benzene.

Our data support the singlet-state isomerization mechanism for dyes I and II in benzene. Since excited singlet states involved are too short-lived to be intercepted by molecular oxygen, we can place upper limits on their lifetimes. In air-saturated benzene solution the oxygen concentration is 1.5×10^{-3} M[26,27] and in oxygen-saturated benzene the oxygen concentration is 7.25×10^{-3} M.[28] Ware has shown that, because of

Table II. Initial Changes in Absorbance[a,b] Following Flash Excitation of Dyes I and II in Heavy-Atom Solvents

		Flash discharge energy, J		
Solvent[c,d]	Solutes	100	156	225
Chlorobenzene	Dye I	0.272 ± 0.003	0.407 ± 0.004	0.547 ± 0.005
Chlorobenzene	Dye I, air	0.264 ± 0.002	0.396 ± 0.011	0.540 ± 0.002
Chlorobenzene	Dye I, benzanthrone	0.417 ± 0.007	0.614 ± 0.010	0.800 ± 0.005
Chlorobenzene	Dye I, benzanthrone, air	0.276 ± 0.003	0.408 ± 0.003	0.548 ± 0.003
Bromobenzene	Dye I	0.266 ± 0.005	0.404 ± 0.005	0.543 ± 0.004
Bromobenzene	Dye I, air	0.254 ± 0.004	0.396 ± 0.003	0.529 ± 0.006
Iodobenzene	Dye I	0.292 ± 0.006	0.428 ± 0.007	0.577 ± 0.005
Iodobenzene	Dye I, air	0.286 ± 0.003	0.425 ± 0.014	0.561 ± 0.003
Chlorobenzene	Dye II	0.208 ± 0.003	0.306 ± 0.003	0.405 ± 0.003
Chlorobenzene	Dye II, air	0.198 ± 0.003	0.294 ± 0.002	0.397 ± 0.004
Chlorobenzene	Dye II, benzanthrone	0.374 ± 0.003	0.529 ± 0.006	0.667 ± 0.003
Chlorobenzene	Dye II, benzanthrone, air	0.212 ± 0.003	0.314 ± 0.002	0.413 ± 0.003
Bromobenzene	Dye II	0.208 ± 0.003	0.312 ± 0.003	0.399 ± 0.006
Bromobenzene	Dye II, air	0.196 ± 0.002	0.293 ± 0.003	0.383 ± 0.003
Iodobenzene	Dye II	0.189 ± 0.003	0.289 ± 0.003	0.387 ± 0.009
Iodobenzene	Dye II, air	0.184 ± 0.003	0.284 ± 0.002	0.374 ± 0.004

[a] The changes in absorbance were measured at 522, 524, and 526 nm for dye I in chlorobenzene, bromobenzene, and iodobenzene, respectively, and at 638, 641, and 645 nm for dye II in these same, respective solvents. [b] Each entry is the average of five to seven measurements. [c] The concentration of each dye solution was 2×10^{-5} M. [d] When employed, the concentration of benzanthrone was 2×10^{-5} M.

the high diffusibility of oxygen, diffusion-controlled reactions involving molecular oxygen occur with a bimolecular rate constant of 3×10^{10} M^{-1} s^{-1}.[29] By proceeding on the assumptions that the dye singlets would be quenched at the diffusion-controlled rate and that as little as 2% quenching would be detected, the lowest excited singlet state leading to isomerization must have a lifetime of less than 5×10^{-10} s for dye I, where the air-saturated solution was used, and 1×10^{-10} s for dye II, where the oxygen-saturated solution was used.

The sensitizer benzanthrone also was used in chlorobenzene solutions; again, relative to the absence of sensitizer, there were substantial increases in the quantity of transient produced following flash excitation of solutions having dyes I and II. Upon saturation of the solutions with air, however, the measured changes in absorbance are reduced, but not quite down to the levels of the air-saturated solutions containing no sensitizer. The differences in behavior for benzene and chlorobenzene dye solutions under these conditions can be explained in terms of differences in oxygen solubilities. Oxygen is less soluble in chlorobenzene than in benzene, so in the former solutions there will be less oxygen available for intercepting benzanthrone triplets.[30,31] It appears that in air-saturated chlorobenzene solutions containing benzanthrone and either dye I or dye II, a small quantity of the benzanthrone triplets escape quenching by oxygen and, instead, deliver their energy to the dyes in an energy-transfer process. Another factor to consider is the possibility that the yield of benzanthrone triplets rises in chlorobenzene relative to benzene and thus increases the number of sensitizer triplets available for energy transfer to dye.

The question arises as to why the use of progressively heavier atoms in the halogenated series of solvents does not lead to greater yields of dye triplets and thus larger quantities of intermediates quenchable by oxygen.[32] The answer is that changing the heavy atom from Cl to Br to I may indeed lead to greater efficiency of triplet-state formation of the dyes. The heavier halogen atoms, however, also tend to make the dye triplets less susceptible to oxygen quenching by shortening their lifetimes and thus decrease isomerization yield. Furthermore, oxygen is less soluble in chlorobenzene than in benzene.[31] Although we did not locate data on oxygen solubility in the other halogenated solvents, if the trend of lower oxygen solubility were to continue for bromobenzene and iodobenzene, there would be less oxygen available in these solvents for quenching of dye triplets.

As summarized in Table II, the measurements carried out with the dyes dissolved in the halogenated solvents included flash-discharge energy as a variable; changes in absorbance were recorded at three different flash-discharge energies. With dyes I and II in chlorobenzene, Figures 3 and 4 show the respective plots of $1/\Delta A$ vs. $1/I$ in degassed and air-saturated solutions, both in the presence and the absence of benzanthrone sensitizer. The four plots of Figure 3 all extrapolate to nearly the same intercept, but in Figure 4 three distinct intercepts are clearly evident. Most likely these differences in intercept are due to differences in the photostationary-state isomer compositions for isomerization via the singlet and triplet states of dye II. The singlet-state contribution to dye isomerization should be greatest when no sensitizer is present in the dye solution; the two plots of Figure 4 for degassed and air-saturated dye solution without sensitizer, respectively, have very nearly the same intercept. The triplet contribution to isomerization of dye II must be greatest in the degassed dye solution with sensitizer present. Experimental error may be involved in the Figure 4 plots, because the intercept for the air-saturated dye solution with sensitizer would be expected to be intermediate between the other two intercepts and this is not the case.

Despite the fact that we do not know how the absorption spectra of the less-stable dye isomers shift in going from benzene to chlorobenzene, a comparison of the intercepts first between Figures 1 and 3 and then between Figures 2 and 4 for dyes I and II, respectively, is in order. All plots in Figures 1 and 3 have essentially a common intercept near 0.3; when appropriately plotted, this is also true for the two sets of data involving dye I that are included in Table I but not in Figure 1. Close to 0.6 are the intercepts for the two plots of Figure 2, the three sets of appropriately plotted data involving dye II that are included in Table I but not in Figure 2, and the two plots of Figure 4 involving dye solution without sensitizer. The shift of the intercept in Figure 4 for the plots relating to the dye II solutions with sensitizer present suggests that the isomerization quantum yields for the triplet state of dye II are sensitive to the change of solvent from benzene to chlorobenzene.

The influence of intramolecular heavy atoms upon the path of the isomerization also was checked by running experiments with dyes III and IV, whose structures are shown below. It is

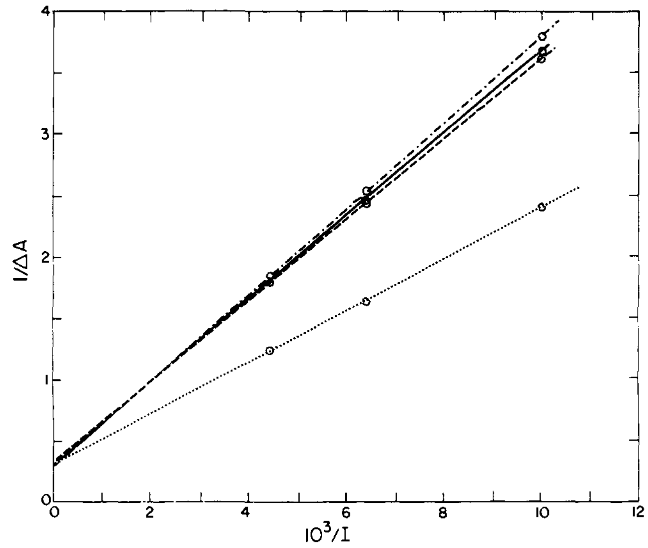
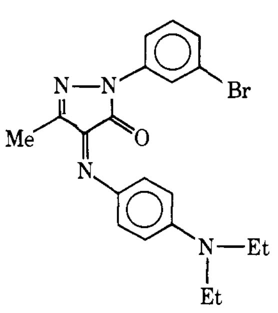
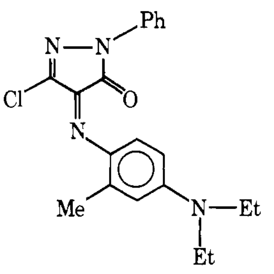


Figure 3. Plots of $1/\Delta A$ vs. $1/I$ for dye I in chlorobenzene solution. The four lines are as follows: (—) degassed solution; (- - - -) air-saturated solution; (·····) degassed solution with sensitizer; and (- · - · -) air-saturated solution with sensitizer.



III



IV

assumed that, as in dye II, the syn configuration for these two pyrazolone azomethine dyes also is the more stable. As things turned out, there were some important differences between these dyes. The behavior of dye III was much the same as that of dyes I and II in that the quantity of anti isomer produced in benzene solution following flash excitation was independent of the presence of dissolved oxygen. Dye IV, which has a chlorine atom rather than a bromine atom, apparently makes more efficient use of the heavy-atom properties of its halogen atom. The quantity of dye isomer generated upon flash excitation of dye IV is measurably greater than when the experimental solution is saturated with air and a further reduction can be effected by saturation with oxygen. To demonstrate the reversibility of the oxygen effect in dye IV, a solution was initially degassed, next saturated with air, then saturated with oxygen, and finally resaturated with air. The quantity of dye transient in air-saturated solution was the same within experimental error before and after the oxygen saturation. Results for these two dyes are summarized in Table III and plots of the corresponding data are shown in Figures 5 and 6.

What the data for dyes III and IV illustrate, first of all, is a positional dependence of heavy-atom substitution. Despite the fact that a bromine atom has a substantially larger atomic weight than a chlorine atom, the latter atom in dye IV is far more effective in influencing the photophysical processes in the pyrazolone dye system than is the former in dye III. A likely reason for this is the fact that the phenyl ring to which the bromine atom in dye III is attached is insulated from the dye chromophore with a saturated nitrogen atom. The chlorine atom in dye IV, by contrast, is attached directly to the dye chromophore and is adjacent to the important carbon–nitrogen double bond about which dye isomerization occurs.

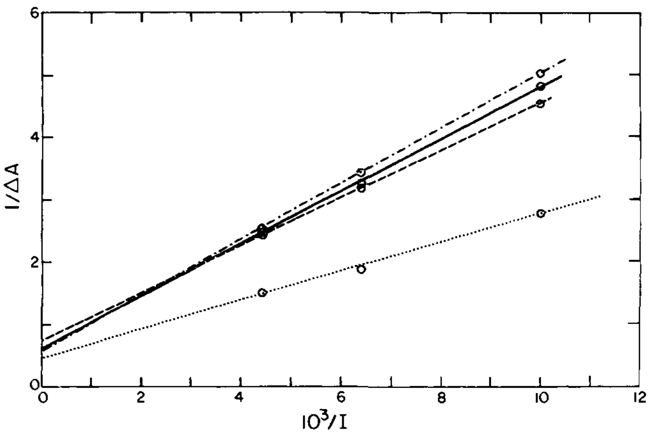


Figure 4. Plots of $1/\Delta A$ vs. $1/I$ for dye II in chlorobenzene solution. The four lines are as follows: (—) degassed solution; (- - - -) air-saturated solution; (·····) degassed solution with sensitizer; and (- · - · -) air-saturated solution with sensitizer.

A positional dependence of heavy-atom substitution in the isomerization of stilbene had been reported by Saltiel and co-workers.[33] They claimed that a bromine atom in stilbene enhances intersystem crossing to the triplet manifold when bonded in a para position, but is ineffective in this respect when moved to a meta position. A more recent publication from Saltiel's laboratories presents evidence that the original conclusion was false and a bromine atom in the meta position of stilbene is indeed effective in promoting intersystem crossing.[34] In comparing stilbene with our pyrazolone dye system, the meta and para positions in stilbene are both part of stilbene's π-electron system, whereas, in pyrazolone dyes, the same is true for the position of chlorine-atom substitution in dye IV, but not for the position of bromine-atom substitution in dye III.

It is possible to make certain estimates concerning the lifetimes of the triplet states in our azomethine dyes. In dye IV, the quantity of photoconversion to the less-stable isomer has been measured under three experimental conditions: degassed, air-saturated, and oxygen-saturated benzene solution. The data from these measurements afford the possibility of a Stern–Volmer analysis and plot[35] based upon the following reaction scheme.

$$^1\mathrm{D} \xrightarrow{h\nu} {}^1\mathrm{D}^* \tag{6}$$

$$^1\mathrm{D}^* \xrightarrow{k_1} {}^1\mathrm{D} \tag{7}$$

$$^1\mathrm{D}^* \xrightarrow{k_2} {}^3\mathrm{D}^* \tag{8}$$

$$^3\mathrm{D}^* \xrightarrow{k_3} {}^1\mathrm{I} \tag{9}$$

$$^3\mathrm{D}^* \xrightarrow{k_4} {}^1\mathrm{D} \tag{10}$$

$$^3\mathrm{D}^* + {}^3\mathrm{O}_2 \xrightarrow{k_5} {}^1\mathrm{D} + {}^1\mathrm{O}_2 \tag{11}$$

$$^3\mathrm{D}^* + {}^3\mathrm{O}_2 \xrightarrow{k_6} {}^1\mathrm{D} + {}^3\mathrm{O}_2 \tag{12}$$

Here I represents dye isomer and reactions 11 and 12 are identical with eq 1 and 2 described earlier. Let k_q represent the sum of k_5 and k_6 for oxygen quenching of dye triplet. We have shown that the singlet states of the preceding dyes are too short-lived to be quenched by oxygen at the oxygen concentrations we have employed, so we shall be concerned only with oxygen quenching of dye triplets. If we let ϕ_0 represent the

Table III. Initial Changes in Absorbance[a,b] Following Flash Excitation of Dyes III and IV in Benzene

	Flash excitation energy, J		
Solutes[c,d]	100	156	225
Dye III	0.069 ± 0.002	0.105 ± 0.002	0.150 ± 0.002
Dye III, air	0.069 ± 0.001	0.108 ± 0.002	0.150 ± 0.001
Dye III, benzanthrone	0.093 ± 0.002	0.145 ± 0.002	0.195 ± 0.002
Dye III, benzanthrone, air	0.070 ± 0.002	0.110 ± 0.003	0.150 ± 0.004
Dye IV	0.321 ± 0.006	0.483 ± 0.006	0.648 ± 0.003
Dye IV, air	0.316 ± 0.007	0.475 ± 0.003 (0.479 ± 0.004)[e]	0.641 ± 0.006
Dye IV, oxygen	0.308 ± 0.005	0.459 ± 0.005	0.628 ± 0.007

[a] The changes in absorbance were measured at 640 nm for dye III and 650 nm for dye IV. [b] Each entry is the average of five to seven measurements. [c] The concentration of each dye solution was 2 × 10^{-5} M. [d] When employed, the concentration of benzanthrone was 2 × 10^{-5} M. [e] This value was recorded after saturating a degassed solution with air, then with pure oxygen, and again with air; see text.

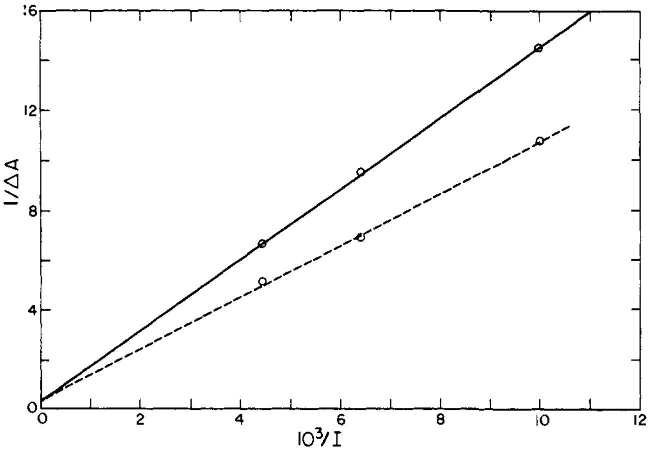


Figure 5. Plots of $1/\Delta A$ vs. $1/I$ for dye III in benzene solution. The solid line corresponds to a degassed solution without sensitizer and the dashed line to a degassed solution with sensitizer.

quantum yield of dye isomer produced in the triplet state in the absence of oxygen and ϕ the quantum yield in the presence of oxygen, then

$$\phi_0 = k_3/(k_3 + k_4) \qquad (13)$$

$$\phi = k_3/(k_3 + k_4 + k_q[O_2]) \qquad (14)$$

$$\phi_0/\phi = 1 + (k_q[O_2]/(k_3 + k_4)) \qquad (15)$$

By letting $\tau = 1/(k_3 + k_4)$, the dye triplet lifetime in the absence of oxygen, this last equation simplifies to

$$\phi_0/\phi = 1 + k_q\tau[O_2]. \qquad (16)$$

According to this equation, a plot of ϕ_0/ϕ vs. oxygen concentration should yield a straight line whose slope is equal to $k_q\tau$.

A Stern-Volmer plot of the data of Table III involving dye IV yields Figure 7 which, obviously, has curved rather than straight lines. This is most likely due to the fact that we do not know how effectively k_2 competes with k_1, so that even though we know that some dye triplet is produced, we do not know how much. We know that in the absence of heavy atoms the dye isomerization is exclusively a singlet-state reaction; it is not to be expected that heavy atoms change the course of the reaction completely to the triplet state. In reality we have the situation described by Shetlar, where two excited states are reactive and only one is quenched;[36] when this obtains, curvature in a Stern-Volmer plot is to be expected. To apply the Stern-Volmer treatment as we have formulated it in eq 6-16, one must have a measure of the quantum yield of transient formation through the triplet state. Since the Stern-Volmer plots involving the triplet states alone are supposed to be linear, one can by trial and error construct such plots for different assumed values of triplet conversion until one obtains the best approximation to a straight line. One will then also have as a bonus an estimate of the extent of intersystem crossing that occurred because of the heavy atom. This has been carried out with the result that the best plot obtains when one assumes that 7% of

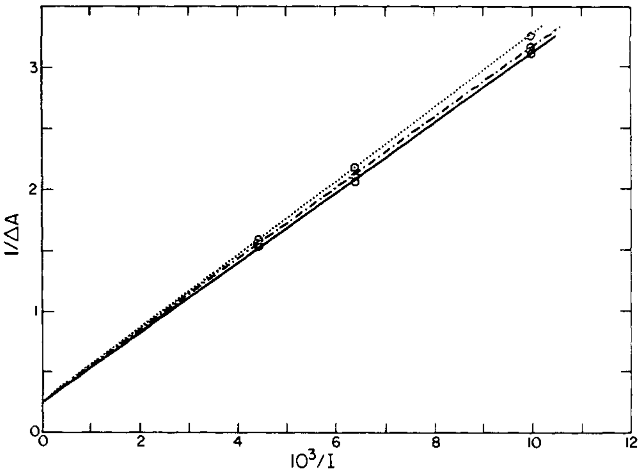


Figure 6. Plots of $1/\Delta A$ vs. $1/I$ for dye IV in benzene solution. The three lines are as follows: (—) degassed solution; (- - - -) air-saturated solution; and (·····) oxygen-saturated solution.

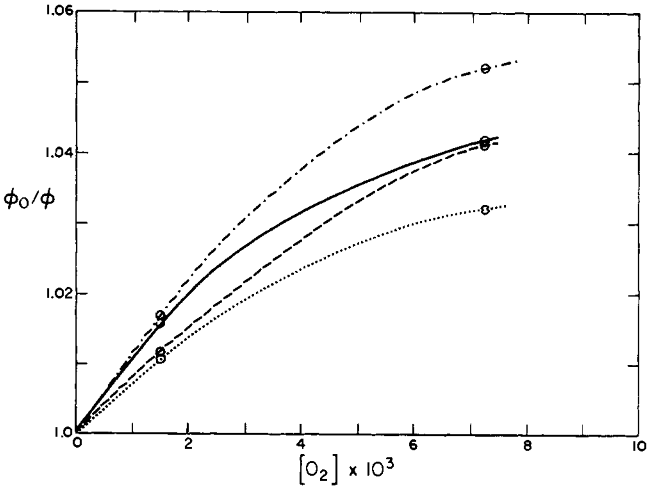


Figure 7. Attempted Stern-Volmer plots for the data for dye IV as reported in Table III. The four lines are as follows: (—) 100-J flash data; (- · - ·) 156-J flash data; (·····) 225-J flash data; and (- - - - -) plot based on eq 17 (see text).

Table IV. Changes in Absorbance Assigned to Triplet-State Reaction of Dye IV Following Its Flash Excitation in Benzene[a]

	Flash discharge energy, J		
Solutes	100	156	225
Dye IV	0.022 ± 0.006	0.034 ± 0.006	0.045 ± 0.003
Dye IV, air	0.017 ± 0.007	0.028 ± 0.003	0.038 ± 0.006
Dye IV, oxygen	0.009 ± 0.005	0.018 ± 0.005	0.025 ± 0.006

[a] It is assumed (see text) that 7% of the absorbance change recorded in Table III for a degassed solution of dye IV is due to isomerization proceeding through the dye triplet state and that only the dye triplet is quenchable by molecular oxygen. The entries in the top row here correspond to 7% of the observed change in the fifth row of Table III and represent the maximum quantity of dye isomer produced in the triplet state. Rows 2 and 3 correspond to the remaining triplet contribution to dye isomerization following partial triplet-state quenching in air-saturated and oxygen-saturated solutions, respectively.

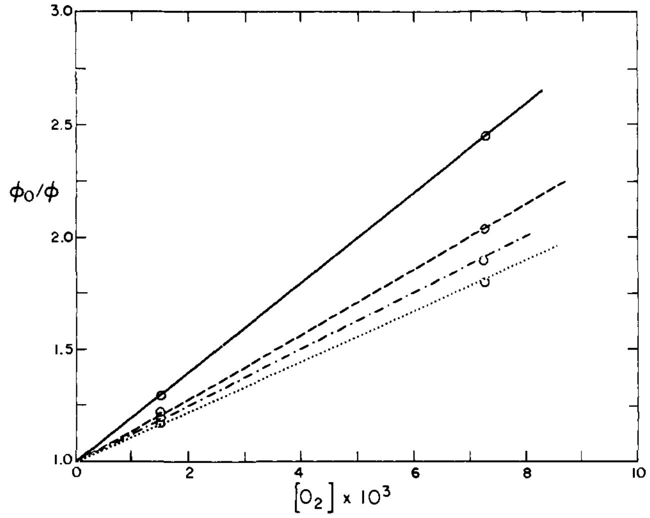


Figure 8. Stern–Volmer plots for the data of Table IV. The four lines are as follows: (—) plot of 100-J flashes; (- - - -) plot for 156-J flashes; (·····) plot for 225-J flashes; and (- - - - -) average values for previous three plots.

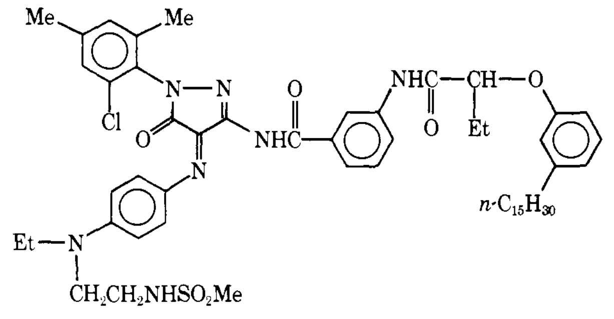
the observed dye isomer is formed in the triplet state. Table IV shows the data, derived from Table III, for the absorbance changes due to isomer formation in the triplet state based upon 7% of the total originally measured in degassed solution; since differences between large numbers are involved, the error range is also large. As shown in Figure 8, lines with somewhat different slopes are obtained for each of the three different light intensities. Since one would expect the slope to be independent of light intensity, the ratios of ϕ_0/ϕ at the different light intensities have been averaged and the resulting average values construct what we consider to be the most reliable straight line. The slope of this line, equal to $k_q\tau$, is 1.4×10^2. As noted earlier, oxygen quenching of dye triplets should proceed at a maximum of near one-half that of a diffusion controlled reaction with a corresponding rate constant of 1.5×10^{10} M^{-1} s^{-1}.[29] If it is now assumed that oxygen quenches the triplet of dye IV at one-half the diffusion-controlled rate, then the lifetime τ of the dye triplet state in the absence of oxygen can be estimated to be approximately 1×10^{-8} s. This lifetime should be taken as a number to the nearest order of magnitude; because of the nature of the estimates involved in its determination, it could be off by as much as a factor of three or four. Since heavy atoms facilitate intersystem crossing and thus reduce triplet lifetimes, this value would represent a lower limit for the triplet lifetime of a pyrazolone azomethine dye in the absence of heavy atoms.

As another check on the validity of the foregoing method as well as our conclusion that the quenching of dye IV isomer formation occurs only in the triplet state but not in the singlet state, we have added to Figure 7 a plot of our data according to a form of the Stern–Volmer equation given by Shetlar.[36] This equation is shown below,

$$\phi_0/\phi = (1 + BQ)/(1 + N_sBQ) \qquad (17)$$

where B is equal to $k_{Q}\tau$, Q is quencher concentration, and N_s is that fraction of reaction that occurs in the singlet rather than the triplet state. We have used our assumed value of N_s and the $k_Q\tau$ value measured from Figure 8 to construct the dashed-line plot in Figure 7; agreement with the other Stern–Volmer plots of Figure 7 is reasonable.

Whereas we report here that molecular oxygen in solution quenches only azomethine dye triplets but not dye singlets, there is another report by Smith, Herkstroeter, and Eddy that under different experimental conditions with different dyes, molecular oxygen can quench not only lowest excited dye singlets and triplets, but also higher excited singlet and triplet states as well.[37] We decided to check to see whether results were consistent between the two studies. To do this, we selected one dye and one solvent employed by Smith et al.[37] and subjected them to our experimental investigations. Dye V, illustrated below, was selected along with mixed tritolyl phosphates as solvent. Benzene also was employed as a solvent for dye V in order to compare better the results obtained with dye V with those of the previous four dyes.



V

The changes in absorbance following flash excitation of dye V in benzene and tritolyl phosphates were measured at three different light intensities, both in the absence and presence of sensitizer and in degassed and air-saturated solution. Results are summarized in Table V and the plots of $1/\Delta A$ vs. $1/I$ corresponding to benzene and tritolyl phosphates solvents are given in Figures 9 and 10, respectively. We do, indeed, observe that molecular oxygen reduces the quantity of dye transient formed relative to the degassed solution, but this effect is significantly larger in tritolyl phosphates than in benzene; in benzene the effect is small and within the range of experimental error. Air saturation of the benzene solution of dye V with sensitizer present does not reduce the level of transient production to that in the absence of sensitizer. The corresponding comparison with air-saturated tritolyl phosphates as solvent has the solution with sensitizer producing markedly less dye isomer than when sensitizer is absent.

Table V. Initial Changes in Absorbance[a,b] Following Flash Excitation of Dye V

Isolvent	Solutes[c,d]	Flash excitation energy, J		
		121	156	225
Benzene	Dye V	0.0191 ± 0.0006	0.0244 ± 0.0005	0.0348 ± 0.0006
Benzene	Dye V, air	0.0189 ± 0.0007	0.0242 ± 0.0003	0.0345 ± 0.0006
Benzene	Dye V, benzanthrone	0.0823 ± 0.0011	0.1026 ± 0.0009	0.1421 ± 0.0021
Benzene	Dye V, benzanthrone, air	0.0214 ± 0.0006	0.0274 ± 0.0005	0.0391 ± 0.0009
TTP[e]	Dye V	0.0262 ± 0.0006	0.0344 ± 0.0006	0.0498 ± 0.0017
TTP	Dye V, air	0.0225 ± 0.0007	0.0290 ± 0.0005	0.0422 ± 0.0009
TTP	Dye V, benzanthrone	0.0599 ± 0.0023	0.0787 ± 0.0010	0.1086 ± 0.0012
TTP	Dye V, benzanthrone, air	0.0211 ± 0.0010	0.0271 ± 0.0009	0.0390 ± 0.0006

[a] The changes in absorbance were measured at 613 nm in benzene and 625 nm in tritolyl phosphates. [b] Each entry is the average of five to seven measurements. [c] The concentration of each dye solution was 2×10^{-5} M. [d] When employed, the concentration of benzanthrone was 2×10^{-5} M. [e] TTP is an abbreviation for tritolyl phosphates.

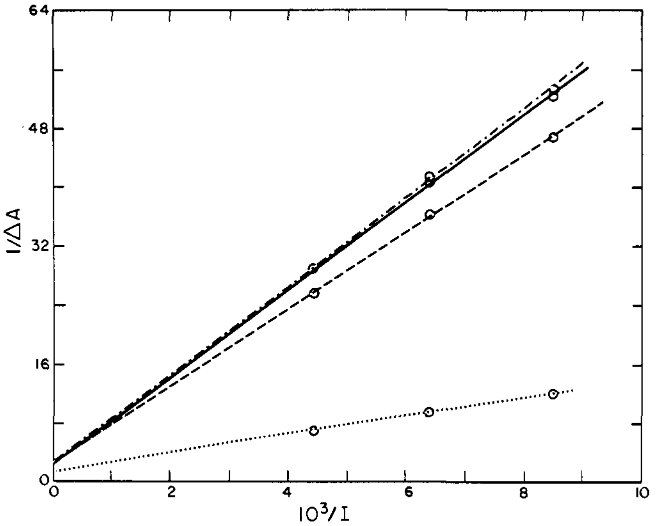


Figure 9. Plots of $1/\Delta A$ vs. $1/I$ for dye V in benzene solution. The four lines are as follows: (—) degassed solution; (- - - -) air-saturated solution; (·····) degassed solution with sensitizer; and (- - - - -) air-saturated solution with sensitizer.

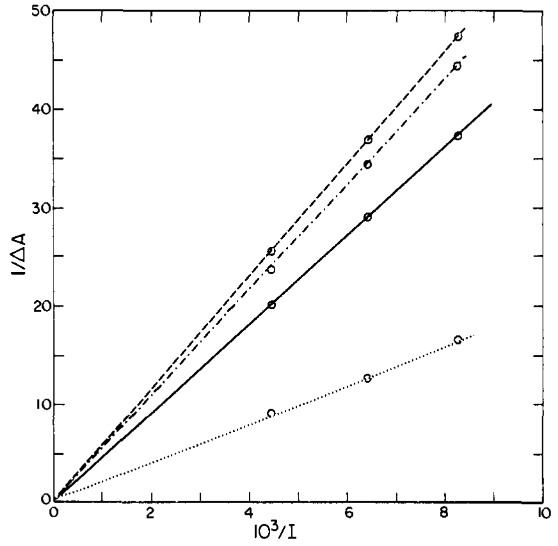


Figure 10. Plots of $1/\Delta A$ vs. $1/I$ for dye V in mixed tritolyl phosphates solution. The four lines are as follows: (—) degassed solution; (- - - -) air-saturated solution; (·····) degassed solution with sensitizer; and (- - - - -) air-saturated solution with sensitizer.

The quenching by oxygen of dye isomer formation in the benzene solution of dye V without sensitizer is so small as to be within experimental error of no quenching; as such these results are consistent with our observations involving dyes I, II, and III in benzene solution. In tritolyl phosphates solution, however, the quenching of dye V isomer formation upon saturation of the solution with air is substantial and, from the results of Smith et al.[37] would be attributed at least partially to interception of the lowest excited singlet state.

A question to be raised in analyzing these data is whether the sulfur and chlorine atoms in dye V as well as the phosphorous atoms in the tritolyl phosphates solvent function as heavy atoms to assist in dye triplet formation. The sulfur and chlorine atoms, by virtue of their isolation from the dye V chromophore, probably cannot serve effectively to catalyze intersystem crossing. If these atoms did so, then one would expect some dye V triplet formation in benzene without sensitizer present and partial quenching of dye isomer formation upon saturation of the solution with air; this is not the case, at least not to any significant extent. In the tritolyl phosphates solvent the phosphorous atom may help to bring about intersystem crossing in dye V. In the absence of sensitizer we see oxygen quenching of dye isomer formation in this solvent, but our experimental method does not tell us in this case whether we are quenching dye singlet, dye triplet, or both. The investigation by Smith et al.[37] requires that states in both manifolds are being quenched and this in turn requires their intermediacy en route to the less-stable isomer of dye V. Because little or no dye V triplet was formed in benzene, it seems reasonable to propose that dye V triplet is formed in tritolyl phosphates solvent because of the "heavy" phosphorous atom.

Now the question to be asked is why the oxygen in air-saturated tritolyl phosphates solution quenches dye V singlets, but the oxygen in air-saturated benzene solution does not. Although we have not measured oxygen solubility in tritolyl phosphates nor have we found it reported in the literature, the simplest solution to this question would require that air be substantially more soluble in tritolyl phosphates solvent than in benzene. This proposed difference in air solubilities also would explain the fact that on comparing the two dye V solutions with sensitizer, admission of air reduces isomer formation substantially more in tritolyl phosphates solution than in benzene. This reduction by dissolved oxygen of the quantity of dye isomer generated in tritolyl phosphates solution with sensitizer beyond that observed in the air-saturated dye solution without sensitizer can be attributed to competitive absorption of excitation light by the sensitizer.

Experimental Section

Materials. Dyes I, II, and IV were synthesized by oxidative coupling of either benzoylacetanilide or the appropriately substituted 1-phenyl-2-pyrazolin-5-one with 2-amino-5-diethylaminotoluene, potassium ferricyanide being used as the oxidizing agent.[37] Dye III, synthesized in like manner, was obtained from Mrs. P. Kuhrt. Purification of the dyes was by chromatography on Woelm silica gel and/or recrystallization until no impurities could be detected by thin-layer chromatography. 7*H*-Benz[*de*]anthracene-7-one (benzanthrone) was an Eastman practical chemical and was recrystallized three times from ethanol. Benzene was Mallinckrodt Nanograde and was used as received, as was mixed tritolyl phosphates, an Eastman organic chemical. Chlorobenzene, bromobenzene, and iodobenzene were Eastman reagent grade chemicals and were vacuum distilled immediately prior to use.

Procedures. All measurements of the conversion of the dyes to their less-stable geometric isomers were carried out on a flash photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H2O) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inside walls were coated with highly reflective paint (Eastman White Reflectance Coating). The flash-discharge energies were 225, 156, and 100 J, corresponding to a 2-μF capacitor charged to 15, 12.5, and 10 kV, respectively. It was determined that the light intensities of the flash discharges varied linearly with respect to the discharge energy over this range of operation and that for a given voltage charge on the capacitor, the flash intensity was reproducible to within ±2%. Glass color filters (Corning 3391 or 3-74) were placed between the flash lamps and the sample cell holder so as to insure only visible excitation of the dyes. The monitoring source was a quartz-halide 100-W lamp (Osram 64625) powered by a regulated dc power supply (Sorensen QSB12-8). The lamp was mounted in an appropriate housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens, and a ¼-m monochromator (Jarrell-Ash). The monitoring beam, after passing through the sample cell, was focused on the entrance slit of the monochromator. Light intensity as a function of time was measured by means of a photomultiplier tube (RCA 4463) located at the exit slit of the monochromator. The output from the photomultiplier was fed into a cathode-follower amplifier and then into a wide-band digital storage oscilloscope (Nicolet Model 1090). The output voltage of the photomultiplier, read directly in digital form on the oscilloscope screen as a function of time, was linear with regard to the light intensity transmitted by the sample, so that an observed change in voltage following flash excitation could be readily converted mathematically to a change in absorbance in the sample.

The cylindrical Pyrex-glass sample cells were 25 cm long and 15 mm o.d. with flat windows fused to the ends. The cells were connected by side arms to bulbs, where solutions were contained during the degassing procedure. Solutions were degassed by subjecting them to several freeze-pump-thaw cycles on a high-vacuum manifold prior to sealing the sample containers.

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Thione Photochemistry. Intramolecular Cyclization of Aralkyl Thiones from S_2[1]

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Abstract: Excitation of a series of aralkyl thiones into the S_2 (π,π^*) state leads to a formal insertion into the δ position and the formation of cyclopentyl thiols. Excitation into the S_1 (n,π^*) state does not lead to the same products and reaction is very slow. The former reaction may be quenched with biacetyl, but not with up to 2 M piperylene, nor can it be induced with a variety of triplet sensitizers. These and other observations make it probable that S_2 is the reactive state. The reaction may thus be (π,π^*) fast hydrogen abstraction or a concerted $2_\pi + 2_\sigma$ process. Use of a thione with a chiral center in the γ position results in racemization of starting material following excitation into S_1, but not into S_2. With a thione possessing a δ chiral center recovered starting thione is, following S_2 excitation, unracemized.

Intramolecular hydrogen abstraction in excited carbonyl compounds is among the more extensively studied of photic reactions. This transformation, which occurs both in aliphatic and aralkyl substances, was originally reported by Norrish nearly forty years ago.[2a] He then described the cleavage, since termed the (Norrish) type II, which occurs between the β and