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(77) EH results.

Determination of Triplet-Energy Levels in Azomethine Dyes by Energy-Transfer Measurements

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Abstract: Because the triplet-energy levels in azomethine dyes could not be observed directly, we attacked the problem of locating the azomethine dye triplet levels by applying an indirect experimental method. Flash kinetic spectrophotometry was used to measure the rate constants for energy transfer from a graded series of triplet sensitizers to a variety of azomethine dyes. Triplet-energy levels in the dyes can be assigned near that point where the efficiency of the energy-transfer process begins to drop. The results unexpectedly revealed dye triplet states of very low energy. The yellow azomethine dyes derived from pivaloylacetanilide, benzoylacetanilide, dibenzoylmethane, diacetylmethane, and dipivaloylmethane all have triplet energies in the range between 40 and 50 kcal/mol. With sensitizers having triplet energies lower than the dyes, the rate of drop in the efficiency of the energy-transfer process is characteristic of molecules that can twist about an essential double bond in the lowest excited state. The triplet energies of the cyan dyes derived from phenol and 1-naphthol and the magenta dyes derived from 2-pyrazolin-5-one are so low that these dyes quench our lowest energy triplet sensitizers at the maximum rate. The cyan dyes have triplet energies of less than or equal to 21 kcal/mol and the magenta dyes of less than or equal to 23 kcal/mol. Because of these low-energy triplet states in azomethine dyes, electronic energy transfer must be considered to be a contributor to the mechanism of the previously observed quenching of singlet oxygen by azomethine dyes.[1]

The longest lived excited electronic state in an organic molecule is almost always the lowest triplet state. On this basis, the triplet state must be considered to be a likely candidate for the reactive state in molecules that undergo photochemical reactions. Because of the possible role of triplet states in the light-fading reactions of azomethine dyes, one of the goals of our experimental investigations has been to gain information about these dye triplet states.

Several experimental methods failed to allow direct observation of the triplet states in azomethine dyes. To try to determine triplet-energy levels in azomethine dyes, both phosphorescence spectroscopy in rigid solvents at liquid nitrogen temperature and electronic absorption spectroscopy in heavy-atom solvents at room temperature were attempted, but without success. In addition, flash photolysis experiments were attempted to monitor triplet–triplet absorption, but the azomethine dye triplets appear to be too short-lived to permit detection.

To obtain a measure of the triplet energy levels in azomethine dyes, we applied an indirect experimental technique involving the measurement of rates of energy transfer from a graded series of triplet sensitizers to each individual dye. Triplet-energy levels in the dyes can be assigned near that point where the efficiency of the energy-transfer process begins to drop. The rule is that energy transfer from the triplet sensitizer remains diffusion controlled[2] until the sensitizer has less than 3 kcal/mol energy in excess of that required to excite the quencher from the ground state to its lowest triplet state.[3,4] The energy-transfer process is depicted in eq 1, where S is the sensitizer and Q is the quencher or

$$S^{*3} + Q \rightleftharpoons S + Q^{*3} \tag{1}$$

dye. As the energy-transfer step becomes progressively more endothermic, the rate of decrease in the measured rate constant is dependent upon the nature of the quencher. In plots of the logarithm of the measured rate constant vs. the difference in triplet energy between sensitizer and quencher, the final slope is that predicted by the Arrhenius equation provided the quencher remains in its ground-state geometry following its acceptance of excitation energy. With quenchers that can change their geometries concomitantly with the excitation process, the slopes of such plots are shallower than the Arrhenius equation predicts, provided that these geometrical changes lower the energy of the quencher triplet states and thus reduce the energy requirements for their excitation.[3-5] "Nonvertical energy transfer" is the name assigned to this phenomenon.[3,4,6,7] Triplet-energy levels normally refer to molecules in their ground-state geometries.

Lamola reports the utility of the energy-transfer technique for triplet-energy determination, particularly after other methods had either failed or yielded erroneous or equivocal results.[8] Examples of molecules whose triplet energies were determined by energy-transfer measurements are biacetyl,[9] some aliphatic and aromatic azides,[10,11] as well as the geometric isomers of stilbene,[3] α-methylstilbene,[3] and some azastilbenes.[12] Plots of the logarithm of the measured rate constant vs. the difference in triplet energy between sensitizer and quencher yield slopes in accord with the Arrhenius equation when the quenchers are biacetyl and *trans*-stilbene.[3,5] Apparent deviations from this equation obtain for the remaining examples listed above by virtue of "nonvertical energy transfer".

Results and Discussion

Flash Kinetic Spectrophotometry. Flash kinetic spectrophotometry was the experimental technique employed for measurement of rates of energy transfer from a graded series of triplet sensitizers to a group of representative azomethine dyes.[3,13] To apply this technique, one generates sensitizer triplets by flash excitation and then monitors their rate of decay in the absence and in the presence of added dye (quencher). An increase in the first-order depopulation rate of the sensitizer triplets will be proportional to the quencher concentration; the rate constant for energy transfer to the dye can then be derived on the basis of eq 2.

$$\frac{d[S^{*3}]}{dt} = k_d[S^{*3}] + k_q[S^{*3}][Q] + k_s[S^{*3}]^2 \qquad (2)$$

Here k_q is the rate constant for energy transfer (or quenching), k_d is the rate constant for decay of sensitizer triplets in the absence of dye, and k_s is the second-order rate constant for triplet-triplet annihilation of the sensitizer. By the mechanism of eq 1, added dye should have no influence on the second-order term involving k_s. Because low concentrations of sensitizer were employed in the experiments described here, self-quenching of sensitizer triplets is negligible and is not included here. The equation does not include any correction for energy transfer in the reverse direction (the dotted arrow in eq 1), which would make the kinetic analysis complex.

It is important to know whether energy transfer in the reverse direction from excited dye (quencher) to ground-state sensitizer can be eliminated from the kinetic analysis. As has been noted above, no azomethine dye revealed triplet-triplet absorption following its flash excitation. Since our flash apparatus can resolve transients with lifetimes greater than or equal to 1 × 10^{-5} sec, it appears that the lowest excited triplet states in dyes are shorter lived.[14] The combination of such short-lived dye triplets and relatively low sensitizer concentrations in these experiments means that reverse energy transfer should be negligible and need not be included in the kinetic scheme. This lack of reversible energy transfer was verified in several cases by showing that the measured rate constant is independent of sensitizer concentration.

In order to carry out the desired measurements, it was necessary to have a series of triplet sensitizers whose triplet energies span a broad energy range and whose triplet-triplet absorption can be monitored following flash excitation. Such a series of sensitizers is known and has been reported on elsewhere.[15] Table I lists the sensitizers employed, their triplet energies, and the wavelengths where their triplet-triplet absorption was monitored. Since no satisfactory sensitizer with a triplet energy below 23 kcal/mol was available, this value provided the lower limit for energy-transfer measurements.

Energy-Transfer Measurements. Before discussing electronic energy transfer in detail, we shall review why we believe that the quenching of triplet sensitizers by azomethine dyes occurs by this mechanism. The answer is, mainly, that no other mechanism is consistent with the evidence. As measured by ultraviolet-visible absorption spectrophotometry, the experimental solutions were recovered unchanged following the experiments. No transient absorption other than that due to sensitizer triplets and, in some cases, syn-anti isomerization of the dyes[16,17] was observed following flash excitation of the solutions containing sensitizer and dye dissolved in degassed benzene. The metastable dye isomers were much longer lived than the sensitizer triplets and these different species were easily distinguished both optically and kinetically. Added dye increased only the rate of the first-order term for depopulation of the sensitizer triplet but left the second-order term unaffected. Furthermore, it will be shown that, in those cases investigated, the rate constants for energy transfer are a relatively smooth function of the triplet energy of the sensitizers. There is some scatter, but it must be remembered that the error in the rate-constant measurements is on the order of ±25% and that other factors such as steric inhibition to energy transfer[18] and dependence of diffusion rates on molecular size may be involved.[19] Finally, the maximum quenching rate for all dyes is that of a diffusion-controlled reaction; those quenching mechanisms other than energy transfer do not often reach this level of efficiency.[20] It seems unlikely that all these conditions would obtain if the quenching process involved reactions such as electron transfer, hydrogen abstraction, the Schenck "relay" mechanism,[21] and radical or radical ion formation.

Table I. Triplet Sensitizers, Their Energies, and Triplet–Triplet Absorption Maxima

Sensitizer	Triplet energy (E_t), kcal/mol[a]	Wavelength for monitoring triplet–triplet absorption, nm
Chrysene	57.2[b]	555
1,2,5,6-Dibenzanthracene	52.2[b]	542
1,2,3,4-Dibenzanthracene	50.8[b]	615
1,2-Benzanthracene	47.2[b]	485
Benzanthrone	47.0[c]	450 or 680
1,12-Benzperylene	46.2[b]	640
9,10-Dimethyl-1,2-benzanthracene	44.3[d]	640
Anthracene	42.6[e]	424
3,4,9,10-Dibenzpyrene	40.2[f]	728
5-Methyl-3,4,9,10-dibenzpyrene	38.5[f]	735
3,4,8,9-Dibenzpyrene	34.4[f]	525
Anthanthrene	33.8[f]	585
Tetracene	29.3[g]	487
Pyranthrene	26.9[h]	595
Zinc phthalocyanine	26.1[i]	490
Violanthrene	25.0[j]	640
Isoviolanthrene	24.0[k]	590
Pentacene	23.0[l]	498

[a] These values are experimental values unless noted otherwise. [b] E. Clar and M. Zander, *Chem. Ber.*, 89, 749 (1956). [c] Reference 3. [d] M. M. Moodie and C. Reid, *Br. J. Cancer.* 8, 380 (1954). [e] M. R. Padhye, S. P. McGlynn, and M. Kasha, *J. Chem. Phys.*, 24, 588 (1956). [f] B. Muel and M. Hubert-Habart, *Proc. Int. Meet. Mol. Spectrosc., 4th, 1959.* 2, 647 (1962). [g] S. P. McGlynn, M. R. Padye, and M. Kasha, *J. Chem. Phys.*, 23, 593 (1955). [h] Calculated value reported by G. G. Hall, *Trans. Faraday Soc.*, 53, 573 (1957). [i] P. S. Vincett, E. M. Voight, and K. E. Rieckhoff, *J. Chem. Phys.*, 55, 4130 (1971). [j] Calculated value reported in ref 1. [k] Calculated value determined by the same method used for the violanthrene triplet energy as reported in ref 1. [l] Calculated value reported in ref 22.

With benzene as solvent, the rate constants for energy transfer from a series of sensitizers to a group of selected azomethine dyes have been measured at room temperature. The results were unexpected insofar as many of the measured rate constants are larger than originally anticipated and, as such, reveal dye triplet states very low in energy.

With those yellow azomethine dyes derived from pivaloylacetanilide, benzoylacetanilide, dibenzoylmethane, diacetylmethane, and dipivaloylmethane, the triplet energies, lie between 40 and 50 kcal/mol above the ground state. Experimental results for these dyes are shown in Figures 1-11. Table II lists the dye triplet energies in terms of a 4-kcal/mol difference between the estimated upper and lower limits. These estimates should be regarded as more accurate for those cases where the curves are well defined. Where only a few points construct the plots, it is recognized that subsequent determinations may reveal the estimates to be slightly in error.

A limitation of these measurements should be noted for those dyes that have distinct syn and anti isomers. This applies to the dyes derived from benzoylacetanilide and pivaloylacetanilide. Although single isomers predominate in each dye under normal equilibrium conditions, the isomeric

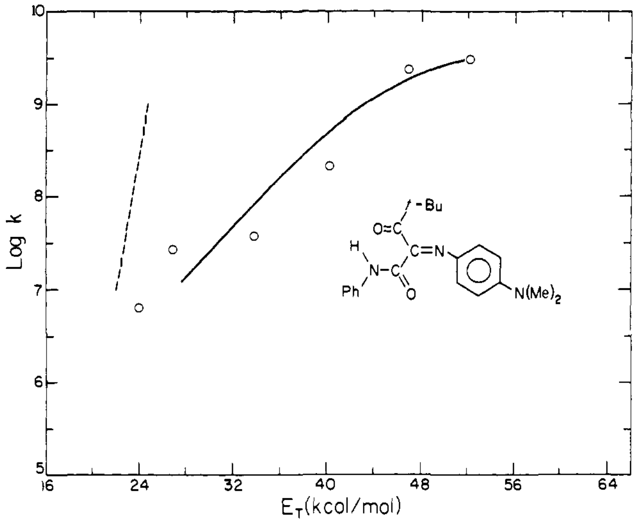


Figure 1. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

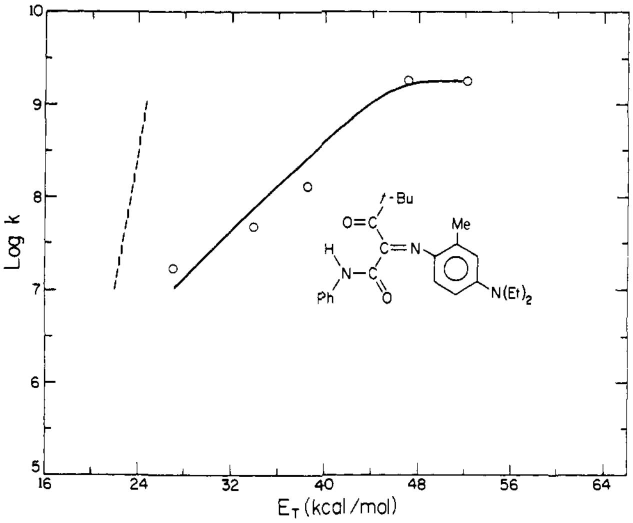


Figure 2. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

equilibrium is perturbed immediately after flash excitation.[16,17] The reestablishment of configurational equilibrium in the dyes is much slower than the energy-transfer process from the sensitizer to the dyes. What is being measured, therefore, for the benzoylacetanilide and pivaloylacetanilide dyes is energy transfer to a mixture of two isomers so that the reported rate constants are composite rate constants. Neither the precise configurational compositions of the dyes under these conditions nor the rate constants for energy transfer to the individual isomers are known. As is evident from the data in Table II and Figures 1-11, however, all the yellow dyes investigated here yield somewhat similar plots and the range between the highest and the lowest triplet energies is approximately 6 kcal/mol. For this reason, it is believed that the syn and anti isomers of the benzoylacetanilide and pivaloylacetanilide dyes do not have very different triplet energies, and that the errors in the respective plots and triplet-energy assignments are not large. However, such differences as are known to exist between the cis and trans isomers of stilbene and α-methylstilbene[3] will be obscured. These problems are absent when the dyes have identical syn and anti isomers.

With dyes derived from phenol, 1-naphthol, and 2-pyrazolin-5-one, results show that, with presently available sensitizers, the dye triplet energies are so low that they can be bounded only from above. The measured rate constants from some of the lowest energy sensitizers to these dyes are diffusion controlled; this is generally accepted as a criterion for the sensitizer having at least 3 kcal/mol energy in excess of that required to excite the quencher to its triplet state. Pentacene, the lowest-energy sensitizer, with a triplet state 23 kcal/mol above the ground state,[22] was employed with the cyan dyes. Since pentacene's triplet-triplet absorption maximum lies at 498 nm, this sensitizer is not well suited for measurements involving magenta dyes. Violanthrene, a sensitizer with a triplet energy of 25 kcal/mol and triplet-triplet absorption at 640 nm,[1,15] was the lowest energy sensitizer that could be employed conveniently with magenta dyes. Tables III and IV list those cyan and magenta dyes that, on the basis of these energy-transfer measurements, can be assigned as having triplet energies less than or equal to 21 and 23 kcal/mol, respectively.

For several of these cyan and magenta dyes, energy-transfer measurements were made with a number of sensi-

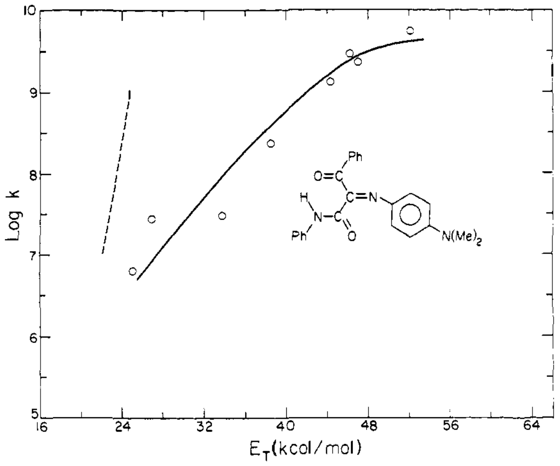


Figure 3. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

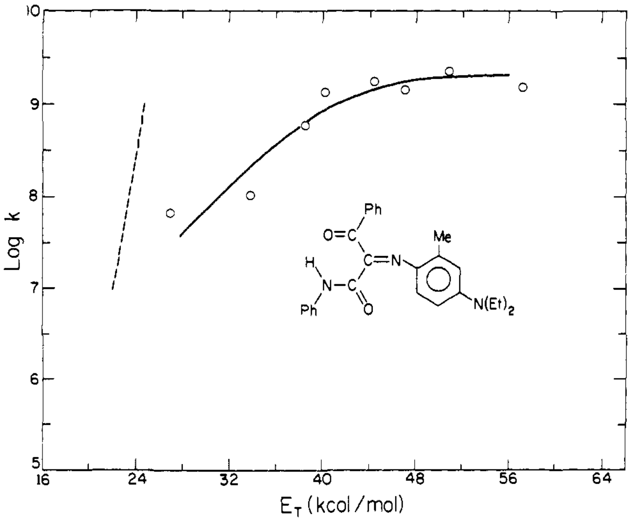


Figure 4. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

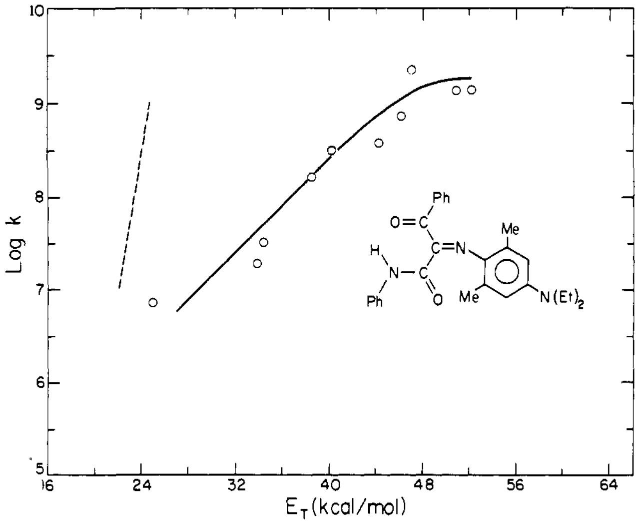


Figure 5. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

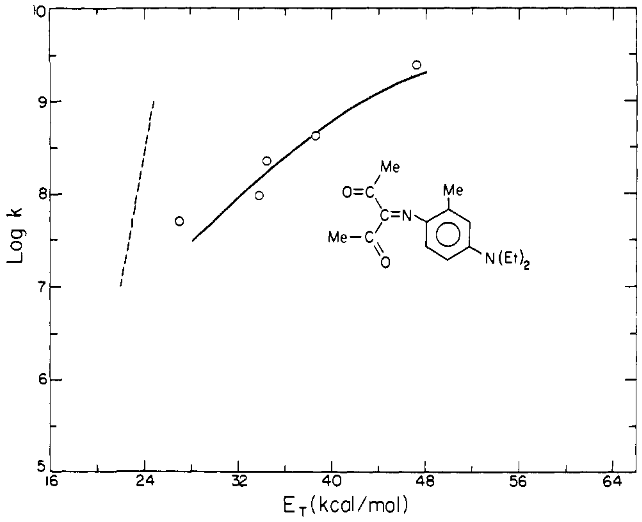


Figure 6. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

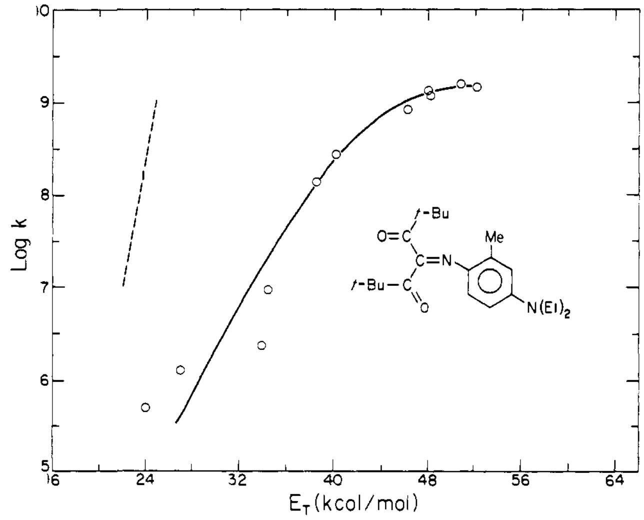


Figure 7. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

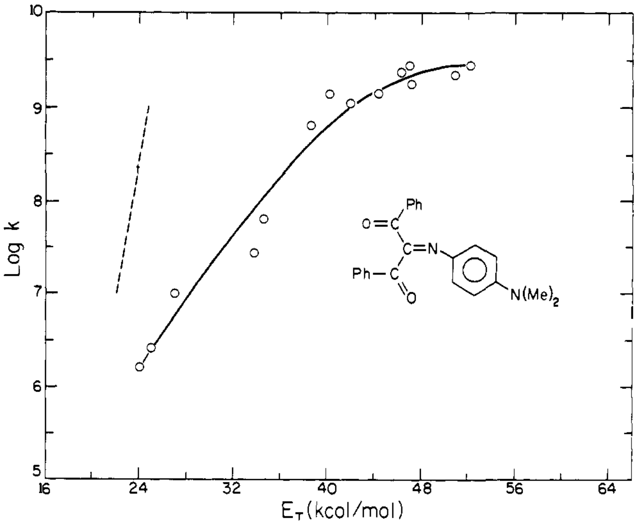


Figure 8. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

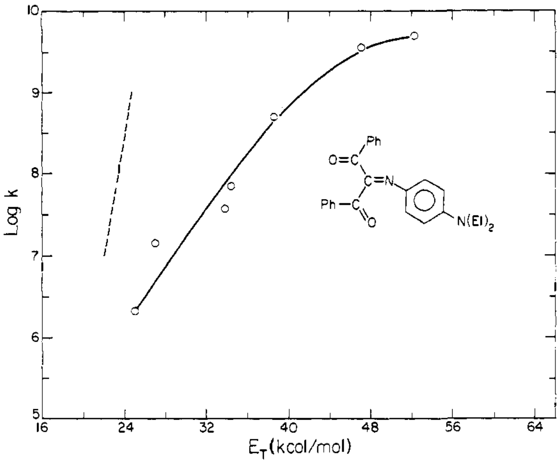


Figure 9. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

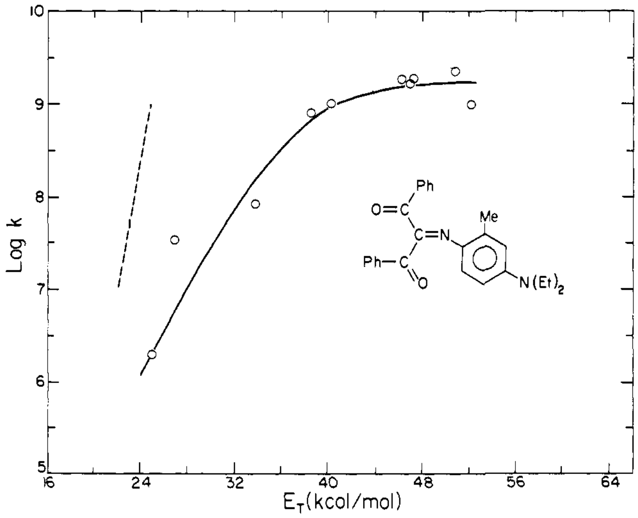


Figure 10. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

Table II. Triplet Energies of Yellow Azomethine Dyes

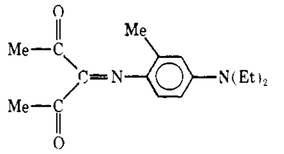
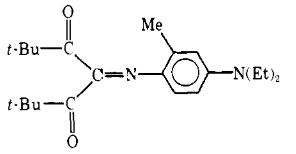
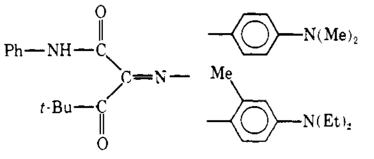
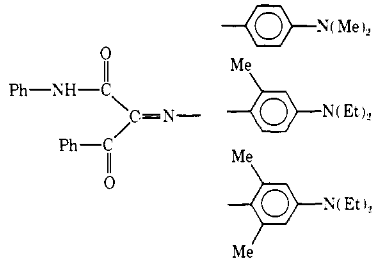
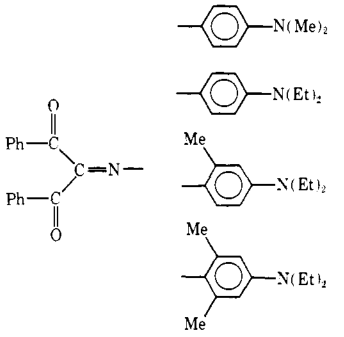
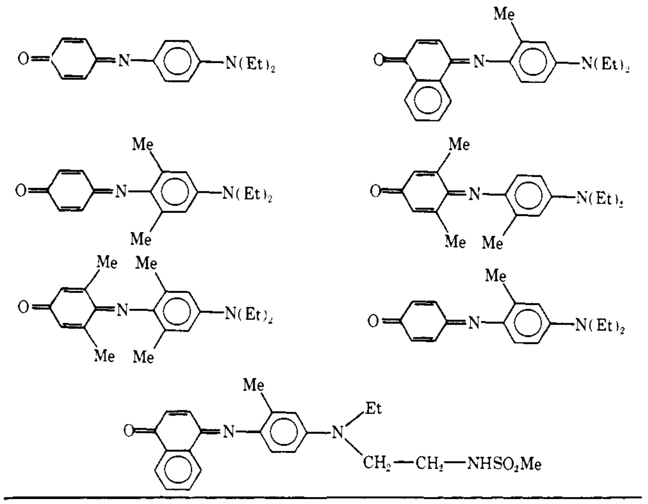
Dye structure	Upper limit, kcal/mol	Lower limit, kcal/mol
	46	42
	47	43
	46	42
	46	42
	45	41
	45	41
	47	43
	46	42
	46	42
	45	41
	46	42

Table III. Dyes Observed to Quench Triplet Pentacene at the Diffusion-Controlled Rate



tizers whose triplet energies cover a broad range of energy. Plots of such data are "flat" in appearance, because the measured rates of energy transfer are all diffusion controlled. Examples are illustrated by Figures 12 and 13.

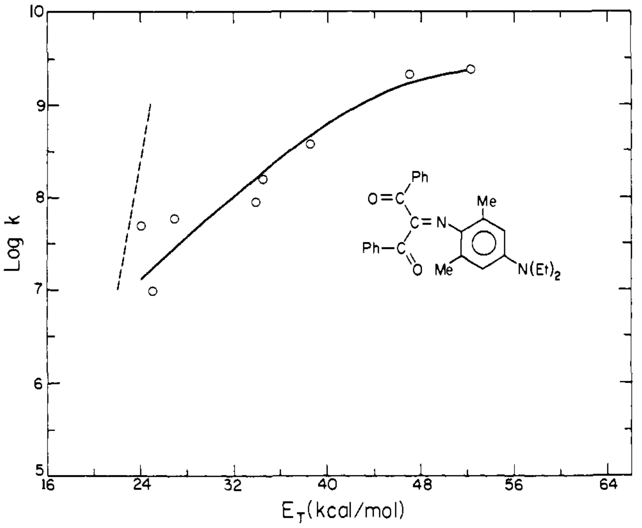
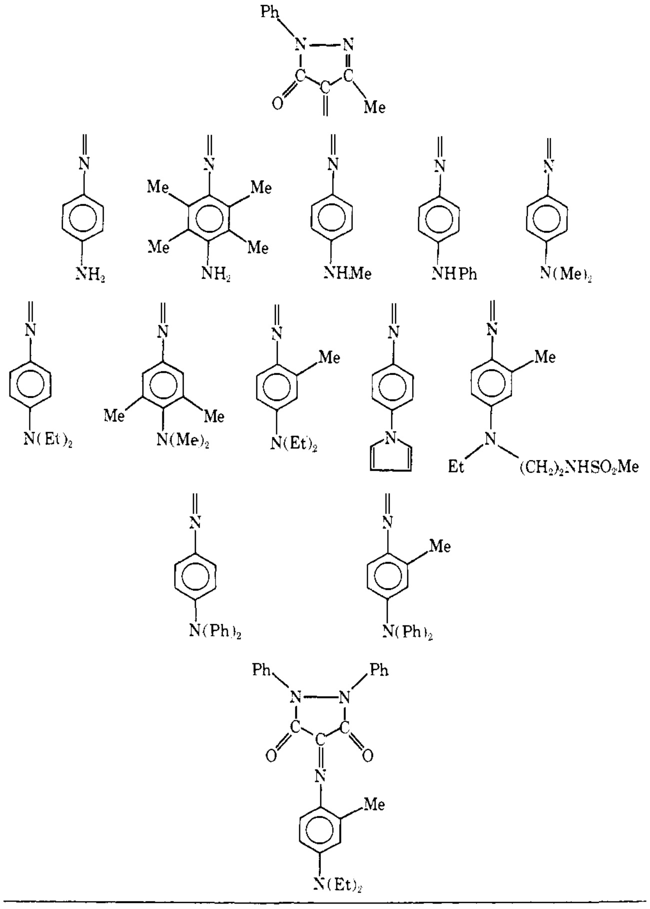


Figure 11. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

Table IV. Dyes Observed to Quench Triplet Violanthrene at the Diffusion-Controlled Rate



As with the nonsymmetrical yellow dyes, there is the problem of quenching by isomeric mixtures when the cyan and magenta dyes do not have identical syn and anti isomers. Even with the lowest energy sensitizers, we have measured diffusion-controlled quenching, and it seems unlikely that either of the individual isomers quench at markedly different rates.

"Nonvertical Energy Transfer." Of significance in each of the plots of Figures 1-11 is the fact that the final slopes

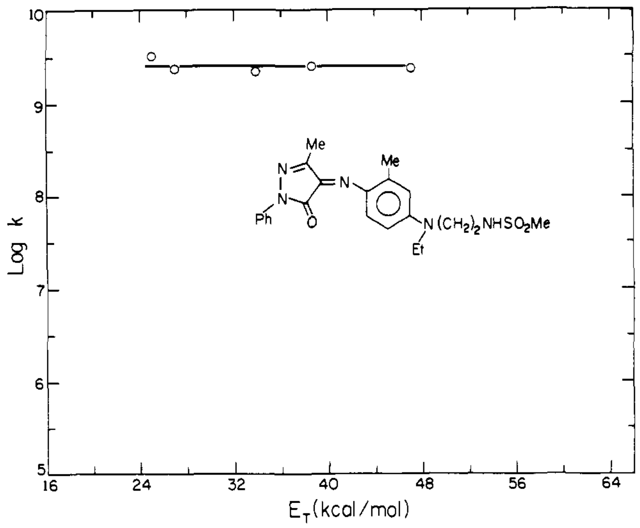


Figure 12. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers.

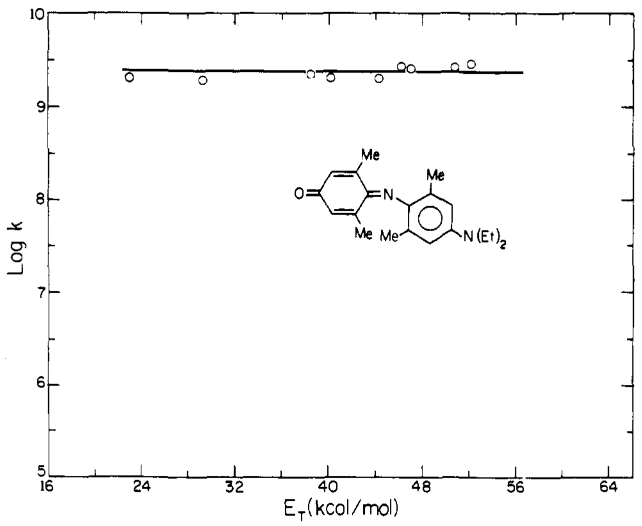
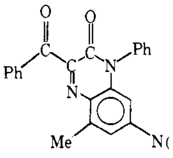
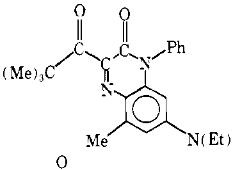
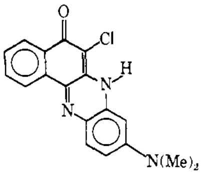


Figure 13. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers.

Table V. Triplet States of Azine Dyes

Dye	Triplet energy, kcal/mol[a]	Triplet lifetime, sec[b]
	44	8.3 × 10^{-5}
	46	7.4 × 10^{-5}
	43	5.0 × 10^{-5}

[a] Based on phosphorescence spectra in glass-forming hydrocarbon solvents at 77 K. [b] The reciprocal of the first-order rate of triplet depopulation in degassed benzene solution at 22°.

are all shallower than the Arrhenius slope of 0.74 kcal^{-1} mol; this latter slope is indicated by the dotted line on the left side of each plot.[5] Until lower energy sensitizers become available, it is not possible to determine whether the plots for the cyan and magenta dyes in the low-energy region will show the same shallow slopes as those for the yellow dyes. Since some of the sensitizers have insufficient energy to excite yellow dyes vertically, these shallow slopes are taken as evidence for "nonvertical energy transfer" to these dyes. The molecules *cis*-stilbene and *cis*- and *trans*-α-methylstilbene undergo "nonvertical energy transfer" by virtue of their ability to isomerize about an essential double bond in the triplet state such that torsion to a geometry intermediate between the cis and trans extremes brings about a lowering of the triplet-state energy.[3,4,6,7] It is known that azomethine dyes with strong electron-donating groups in the para position of the aromatic ring attached to the azomethine nitrogen atom isomerize by torsion about the azomethine bond.[17] Because the stilbene molecules also isomerize by torsion about a double bond, the similarity in behavior between them and the azomethine dyes in undergoing "nonvertical energy transfer" is not unexpected.

Although evidence indicates that twisting about the carbon-nitrogen double bond lowers the triplet energy of the dyes, those triplet energies cited in Table II are for the dyes in their ground-state geometries. The depth of the well in the triplet-energy profile in the twisted state cannot be determined from these data.

Comparison with Azine Dyes. Azine and azomethine dyes are similar in structure, with the distinction that azine dyes have an additional bond with a saturated nitrogen atom that joins the substituents on each side of the azomethine bond. Azine dyes available for this investigation are illustrated in Table V. As is evident, this additional bond holds the azine dyes in a rigid position and prevents any isomerization about the C=N bond. Unlike azomethine dyes, azine dyes show both phosphorescence and triplet-triplet absorption. Table V summarizes appropriate data relating to the azine dye triplet states. The flexibility about the C=N bond in azomethine dyes must be that factor responsible for their failure to luminesce as well as for their short triplet lifetimes. The measurements of energy transfer to the yellow dyes, at least, have already provided evidence that, as the dyes twist about the C=N bond in the triplet state, their triplet energy decreases. We believe that the torsion about the C=N bond in the dye triplet manifold can provide a path for rapid deactivation and shorten triplet lifetimes to the point where they can no longer be observed directly by either phosphorescence or flash photolysis. Others also have proposed that rotation about the C=N bond in azomethine compounds may be an important path for the dissipation of electronic energy.[23-25]

Steric Effects. A number of the yellow azomethine dyes are substituted with alkyl groups that provide steric bulk adjacent to the carbon-nitrogen double bond. As evident from the structures of the dyes listed in Table II, examples of steric crowding on each side of the azomethine bond are included. There are, at least with these yellow dyes, no pronounced trends in measured triplet energies as a function of steric crowding. By contrast, it seems likely that this same type of steric hindrance brings about a reduction of the triplet-energy levels in the magenta and cyan dyes.[1]

Significance. The question arises as to the significance of the low levels and short lifetimes of these lowest excited triplet states in azomethine dyes. As the gap between the ground state and the triplet state narrows, radiationless conversions increase in rate and reduce the lifetime of the triplet state;[26] these two phenomena are thus interrelated. It has been demonstrated by Smith that, in many azomethine dyes, the photochemical reaction most likely takes place, at least in part, in the lowest triplet state.[27] Azine dyes, which, by comparison with their azomethine counterparts, have higher triplet-energy levels, longer triplet lifetimes, and no possibility for torsion about the azomethine bond to a new geometry with an even lower triplet-energy level, show poorer light stability.[27] It appears that the short triplet lifetimes in azomethine dyes serve to limit the extent of any photochemical reactions.

Singlet oxygen, a highly reactive species, lies only 22.5 kcal/mol above its ground state in energy.[28-30] A number of magenta and cyan dyes have been observed previously to be singlet-oxygen quenchers.[1] Since we now know that many magenta and cyan dyes have triplet states of less than or equal to 23 kcal/mol, electronic energy transfer undoubtedly makes a contribution to the mechanism by which these dyes quench singlet oxygen.[1] It is this quenching mechanism that helps to protect cyan and magenta dyes from attack by singlet oxygen.

Experimental Section

Materials. Dyes were synthesized by oxidative coupling of the appropriately substituted β-dicarbonyl compound, 3-methyl-1-phenyl-2-pyrazolin-5-one, phenol, or 1-naphthol with the appropriately substituted *p*-phenylenediamine, potassium ferricyanide being used as the oxidizing agent.[31] Purification was by chromatography on Woelm silica gel and/or recrystallization.

The benzene was Mallinckrodt Nanograde and was used as received.

Chrysene and 1,2,5,6-dibenzanthracene were both Eastman reagent grade and each was purified by sublimation under vacuum. 1,2,3,4-Dibenzanthracene was purchased from the Aldrich Chemical Co. and was purified by chromatography on Woelm silica gel and recrystallized from cyclohexane. 1,2-Benzanthracene was an Eastman reagent chemical that was purified by chromatography on Woelm alumina and recrystallized from ethanol. 7*H*-Benz[*de*]anthracen-7-one was an Eastman practical chemical and was recrystallized three times from ethanol. 1,12-Benzperylene was purchased from Aldrich Chemical Co. and was recrystallized from benzene. 9,10-Dimethyl-1,2-benzanthracene was an Eastman reagent chemical, purified by chromatography on Woelm silica gel. Anthracene was an Eastman scintillation grade chemical and was used as received. The sources and purifications of the remaining sensitizers have been described elsewhere.[15]

Procedures. Kinetic measurements were carried out on a conventional flash photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H20) 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 energy of the flash discharge was 400 J (2-μF capacitor charged to 20 kV). The flash output returned to ⅓ peak intensity within 15 μsec. 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 oscilloscope (Tektronix 555). Oscillographs were photographed with an oscillograph-record camera.

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.

The oscillographs were enlarged to facilitate more precise measurement of the transient phenomena. The lifetimes of sensitizer triplets were measured by the recovery rate of the monitoring beam after the excitation flash. Kinetic analysis was by the method of Linschitz and Sarkanen.[32,33]

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(2) Throughout the text, the term "diffusion-controlled" is employed to signify a reaction involving triplet-energy transfer that is exothermic by 3 kcal/mol or more. It is recognized that, as reported recently, when solvent viscosities are low, this process frequently shows less than unit efficiency owing to the escape of either the triplet sensitizer or the quencher from the solvent cage prior to reaction. This has been reported by P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968), and N. J. Turro, N. E. Schore, H. C. Steinmetzer, and A. Yekta, *ibid.*, **96**, 1936 (1974).

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(5) The Arrhenius equation in logarithmic form is log $k = E_a/2.3RT +$ log A, where k is the measured rate constant, E_a the activation energy, and A the preexponential factor. In the usual application of this equation, one plots log k vs. $1/T$ and obtains a slope equal to $-E_a/2.3R$. We apply the Arrhenius equation in an alternative manner here. If one takes the difference between two values of the above equation, one obtains Δ log $k = -\Delta E_a/2.3RT$. If the deficiency in the energy of the sensitizer triplet to excite the quencher is made up by thermal activation energy, then one can substitute ΔE_T for ΔE_a, where ΔE_T is the difference in triplet energies between sensitizer and quencher. A plot of Δ log k vs. $-\Delta E_T$ would be expected to have a slope of $1/2.3RT$. In practice in the figures, the abscissas and ordinates are labeled E_T and log k, respectively, because these values are measured directly and have the same units as $-\Delta E_T$ and Δ log k, respectively.

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