A Model for the Triplet State Photochemical Isomerization of Azomethine Dyes

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Abstract: Experiments were run to elucidate the mechanism of the triplet state photochemical isomerization about the C═N bond that azomethine dyes undergo. It was necessary to base the determination of the mechanism upon energy transfer measurements from triplet sensitizers to a group of benzoylacetanilide and pyrazolone azomethine dyes selected for the experiments. The energy of the dye triplet state is somewhat dependent upon the para substituent in the aromatic ring attached to the azomethine nitrogen atom; dye triplet energies are highest when the substituents have σ constants near zero, and the dye triplets decrease in energy as the substituent σ constants become either positive or negative. Two isomerization mechanisms were distinguished: torsion about the azomethine bond and inversion about the nitrogen atom. Electron-donating substituents facilitate the former, and electron-withdrawing substituents facilitate the latter. We propose that the shape of the triplet state potential energy surfaces changes with the class of dye. Those dyes derived from benzoylacetanilide, regardless of whether or not the isomerization proceeds by torsion or inversion, have, at geometries intermediate between the syn and anti configurations, deep wells in their triplet potential energy surfaces. By contrast, only shallow wells are present in the triplet state potential energy surfaces of those dyes derived from 3-methyl-1-phenyl-2-pyrazolin-5-one. The ground state potential energy surfaces are, in a sense, mirror images of the triplet state surfaces with the maxima at the intermediate geometries representing the thermal barriers between the syn and anti configurations. Isomerization models predict that dyes, when their preferred triplet configurations are populated, relax by torsion or inversion to the minima in their triplet potential energy surfaces and then intersystem cross to the maxima in the ground state potential energy surfaces followed by a partitioning that populates both geometric dye isomers. The ground state thermal barriers are sufficiently small that the less stable dye isomers cannot be isolated, but instead revert back to the preferred configurations.

Isomerization is known to be an important photochemical reaction in compounds containing the carbon-nitrogen (azomethine) double bond.[1-5] To this class of compounds belong azomethine dyes, used as image dyes in color photography. Because the thermal barriers between the syn and anti isomers are sufficiently small, the less stable isomers cannot be isolated but exist in equilibrium with the isomers in the preferred configurations. In almost all cases investigated, the isomer in the preferred configuration completely dominates the equilibrium at room temperature. Photochemically induced shifts in the isomeric equilibria of azomethine dyes are only temporary and are followed by thermal relaxations to reestablish the initial equilibrium conditions.[4-6]

Two mechanisms are known for the thermal isomerization of azomethine dyes.[1,4,5] The torsion mechanism involves a rotation or twisting about the azomethine bond. To bring about such a change in geometry, there must be a reduction in the double bond character of this bond in the transition state relative to the ground state. On proceeding through the transition state, the C═N—C bond angle remains constant and the sp^2 hybridization of the nitrogen atom electrons does not change. The inversion mechanism provides an alternative path for this change in the geometry of the dye. Rather than a rotation about the azomethine bond, this mechanism involves a shift of the nitrogen substituent from one side of the molecule to the other through a linear transition state where the carbon-nitrogen double bond remains intact. The nitrogen atom electrons rehybridize from sp^2 to sp with the formerly nonbonding electrons becoming available for conjugation with other π-electron systems attached to the nitrogen atom. The mechanism of the thermal isomerization of benzoylacetanilide and pyrazolone azomethine dyes is dependent upon the nature of the substituent in the para position of the aromatic ring attached to the nitrogen atom.[4] With electron-donating substituents, the isomerization proceeds by torsion about the central azomethine bond and, with electron attractors, inversion about the azomethine nitrogen is the preferred path.

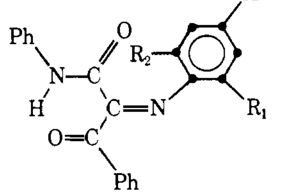
The photochemical isomerization of the azomethine dyes can be brought about in two ways, either by direct absorption of the light by the dyes or with the intermediacy of triplet state photosensitizers that absorb the light energy and transfer it to the dyes.[4,6] This latter process leads to dye isomerization via the triplet state because the dye triplets are populated in the energy transfer process. Elsewhere it is demonstrated that direct light absorption by the dyes leads to isomerization in their lowest excited singlet states.[7]

In this investigation it was our goal to determine both the mechanism of the triplet state dye isomerization and, especially, the relationship between the triplet state and ground state potential energy surfaces with regard to the isomerization.

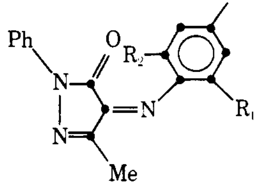
Results and Discussion

The photochemical isomerization of azomethine dyes proceeds at a rate that is too rapid to permit the direct monitoring of the transients involved with our flash photoelectric apparatus. It was necessary, for this reason, to apply alternative experimental methods to the determination of the azomethine dye isomerization mechanism. In this connection, energy transfer measurements from the triplet state photosensitizers provided useful data.

Two series of azomethine dyes were selected for this investigation. These dyes are derived from benzoylacetanilide and 3-methyl-1-phenyl-2-pyrazolin-5-one, as illustrated, with various substituents in the para position of the aromat-



benzoylacetanilide
azomethine dye class
R_1, R_2 = H, Me
X = various substituents



pyrazolone
azomethine dye class
R_1, R_2 = H, Me
X = various substituents

ic ring attached to the azomethine nitrogen atom. The dyes are shown in their preferred ground state configurations, which are syn for both classes of dyes.[8-10]

It is important to know, first of all, just what the triplet energies of the dyes under consideration are. A previous study has dealt with the problem of triplet energy determination in azomethine dyes, but only for those benzoylacetanilide and pyrazoline dyes substituted with electron-donating dialkylamino substituents.[11] Since the dyes under consideration neither phosphoresce nor reveal any absorption intensity assignable to absorption from the ground state to the triplet state, energy transfer measurements turned out to be the only method applicable to the determination of dye triplet energies. Lamola reports the utility of the energy transfer technique for triplet energy determination, particularly after other methods had failed or yielded either erroneous or equivocal results.[12] 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 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.[13,14] For sensitizer and quencher with identical triplet energies, the rate constant for energy transfer is one-half that of a diffusion-controlled reaction.[13] The energy transfer process is depicted in eq 1, where S is the sensitizer and Q is the quencher or dye.

$$S^{*3} + Q \rightleftharpoons S + Q^{*3} \qquad (1)$$

Flash kinetic spectrophotometry was the experimental technique employed for measurement of rates of energy transfer from a graded series of triplet sensitizers to our selected group of azomethine dyes. To apply this technique, one generates sensitizer triplets by flash excitation and then monitors their rate of depopulation in the absence and in the presence of added quencher or dye. 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.

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

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.

It is important to know whether energy transfer in the reverse direction from excited dye (quencher) to ground state sensitizer as indicated by the dotted arrow in eq 1 can be eliminated from the kinetic analysis. 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 the dyes are shorter lived. The combination of such short-lived dye triplets and sensitizer concentrations of 1 × 10^{-5} M or less 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 concentrations.

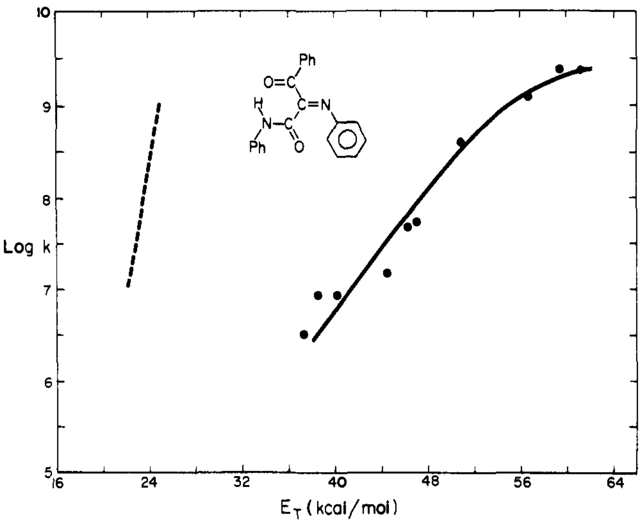


Figure 1. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

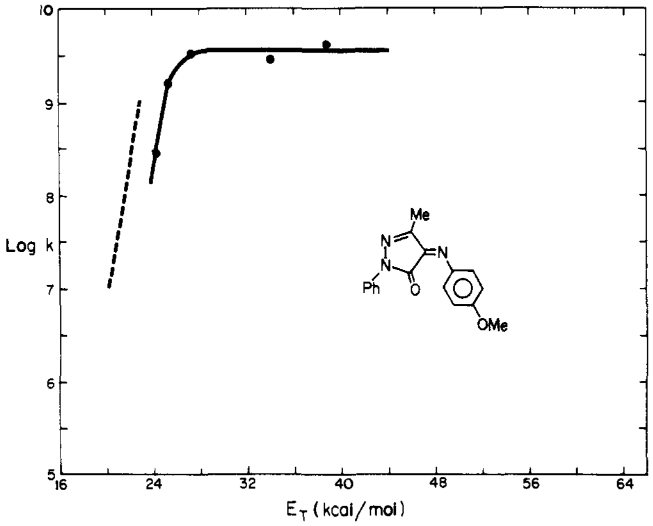


Figure 2. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to the illustrated dye vs. the triplet energies of the sensitizers. The dotted line shows the final slope predicted by the Arrhenius equation.

With benzene as solvent, the rate constants for energy transfer from a series of triplet state photosensitizers to a group of selected azomethine dyes were measured at room temperature. For reasons presented elsewhere,[11] we are confident that the quenching of sensitizer triplets occurs by energy transfer and not by other reactions such as electron transfer, charge transfer, hydrogen abstraction, the Schenck "relay" mechanism,[18] and radical or radical ion formation.

Plots of the logarithms of the rate constants for energy transfer to benzoylacetanilide and pyrazolone azomethine dyes vs. the triplet energies of the sensitizers employed are illustrated in Figures 1 and 2, respectively. So long as the sensitizers have energies well in excess of that required to excite the dyes in their triplets, energy transfer will occur at the diffusion-controlled rate with measured rate constants of approximately 3 to 6 × 10^9 M^{-1} sec^{-1}. The triplet energies of the dyes can be assigned values approximately 3 kcal/mol below the point on the abscissa where the rates of energy transfer to the dyes drop below the diffusion-controlled rate. Table I lists the upper and lower bounds to the triplet energies of these two dyes as well as for seven other dyes whose energy transfer plots, for the sake of brevity, are not included here. The range of several kcal/mol makes allowance for experimental error in the measurements as well as a scarcity of sensitizers over certain parts of the energy

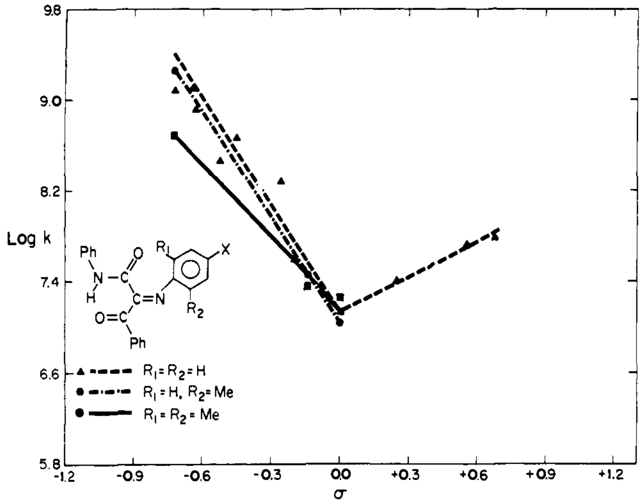


Figure 3. Plot of the logarithm of the rate constants for energy transfer from the sensitizer 9,10-dimethyl-1,2-benzanthracene to different series of benzoylacetanilide dyes vs. the σ constants of the dye substituents.

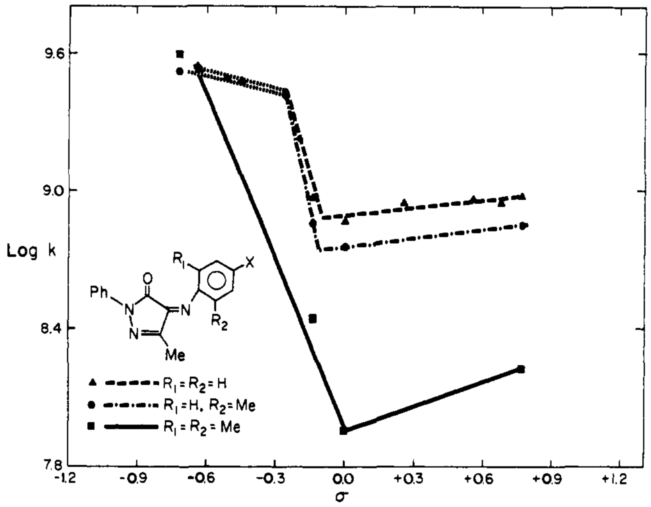


Figure 4. Plot of the logarithm of the rate constants for energy transfer from the sensitizer violanthrene to different series of pyrazolone azomethine dyes vs. the σ constants of the dye substituents.

scale. Those sensitizers employed in carrying out the energy transfer measurements are listed elsewhere.[11]

Complete energy transfer plots were constructed only for a limited number of dyes. In order to attempt a correlation of the dye triplet energies with the substituent σ constants without carrying out the large number of measurements required for complete energy transfer plots for each dye under consideration here, a simplified procedure was used. We plotted the logarithm of the rate constant for energy transfer from the same sensitizer to each dye in the different series of dyes vs. the σ constant of the various dye substituents. Provided the rates of energy transfer are less than diffusion controlled and one has a series of closely related quenchers such that the slopes in the lower energy region of the log k vs. E_T plots are close to each other (vide infra), one can, through comparison of the rates of energy transfer from a single sensitizer, establish on a relative scale the triplet energies of each member of the series of quenchers. Continued increases in the energy requirements of the quencher lead to progressive decreases in the efficiency of the energy transfer process. If the triplet energies of certain of these quenchers are known from other measurements, one can, on the basis of the measured rate constants, estimate the triplet energies of the remaining members of the series.

In the case of the benzoylacetanilide azomethine dyes, 9,10-dimethyl-1,2-benzanthracene was the sensitizer of choice, and the plot of the results in Figure 3 is V shaped. Since the rate of energy transfer will be inversely dependent upon the triplet energy of the dye, it can be stated that the dyes in the series with the highest triplet energies have substituents with σ's near zero; lower triplet energies obtain for those substituents with negative or positive σ constants. Strong electron donors are, however, more effective in reducing the dye triplet energies than are electron withdrawers.

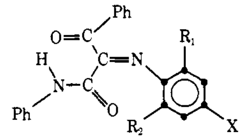
The sensitizer violanthrene was selected for the same type of measurements with those dyes derived from 3-methyl-1-phenyl-2-pyrazolin-5-one. Results of these energy transfer measurements from triplet sensitizers to the various pyrazolone azomethine dyes are plotted in Figure 4. As has been reported elsewhere, the rates of energy transfer from violanthrene to those pyrazolone azomethine dyes substituted with strong electron donors are diffusion controlled; however, no sensitizer with a lower triplet energy could conveniently be employed for measurement of energy transfer to those magenta-colored dyes. If one does not include the data points for diffusion-controlled energy transfer, Figure 4 is also V shaped. If a sensitizer with a sufficiently low energy were available, all data points in the figure would move to lower values along the ordinate and all presumably would fit the V-shaped plot.

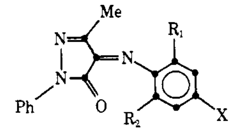
Triplet energies for those dyes included in Figures 3 and 4 are also listed in Table I along with the σ constants for the para substituents in the dyes. Included in the table are triplet energy assignments for the pyrazolone azomethine dyes substituted with strong electron donors; these assignments are based upon an extrapolation of the left leg of the plot in Figure 4 as though the rate constants were not limited by the rate of diffusion. It is noteworthy that, in the pyrazolone dye class, only those dyes with substituents other than strong electron-donating amines have triplet energies that can be measured directly by the energy transfer technique. This limitation arises due to the lack of triplet sensitizers of sufficiently low energy for energy transfer measurements. As illustrated in Figure 2, when the substituent in question is a methoxy group, an energy transfer plot for triplet energy determination can be constructed; the dye triplet energy is, however, just barely high enough to permit this, because the sensitizers involved are the lowest energy ones that we possess.

The foregoing data provide essential information about the triplet energies of the dyes in their preferred configurations. We do not know what the triplet energies of the less stable dye isomers are, but it had been proposed that the triplet energies for each dye do not change by a great deal from the syn to the anti isomer.[11]

Included in Figures 3 and 4 are separate plots for those dyes substituted, respectively, with one and two methyl groups ortho to the azomethine bond linkage. Although an exception is presented below, increasing methyl substitution of this type generally leads to less efficient sensitizer quenching. This behavior can be interpreted in one of two ways. The first is that these methyl groups provide sufficient bulk to hinder sterically the efficiency of the energy transfer process, and the second is that the dyes containing these methyl groups have higher triplet energies than their unsubstituted counterparts. The latter proposal has our support, because both the sterically hindered and the unhindered dyes quench sensitizers with sufficiently high energy triplet states at the diffusion-controlled rate. Furthermore, the illustrated sterically hindered dye has been shown to

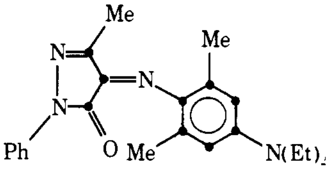
Table I. Triplet State Energy Levels of Azomethine Dyes



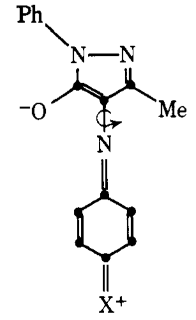
R_1	R_2	X	σ constant for X[a]	Upper limit, kcal/mol	Lower limit, kcal/mol	Basis for energy value assignments
H	H	$N(Et)_2$	−0.72	45	41	*b*
H	H	NHMe	−0.64	45	41	*b*
H	H	$N(Me)_2$	−0.63	46	42	*c*
H	H	NH_2	−0.52	49	45	*b*
H	H	NHPh	−0.45	48	44	*b*
H	H	$N(Ph)_2$	−0.26	51	47	*d*
H	H	OMe	−0.20	57	53	*b*
H	H	Me	−0.14	58	54	*b*
H	H	H	−0.00	61	57	*e*
H	H	Cl	+0.25	58	54	*b*
H	H	COMe	+0.56	57	53	*b*
H	H	CN	+0.68	57	53	*d*
Me	H	$N(Et)_2$	−0.72	43	39	*c*
Me	H	Me	−0.14	58	54	*b*
Me	H	H	0.00	62	58	*b*
Me	Me	$N(Et)_2$	−0.72	47	43	*c*
Me	Me	Me	−0.14	59	55	*b*
Me	Me	H	0.00	60	56	*b*
						
H	H	$N(Et)_2$	−0.72	21	17	*f*
H	H	NHMe	−0.64	22	18	*f*
H	H	$N(Me)_2$	−0.63	22	18	*f*
H	H	NH_2	−0.52	23	19	*f*
H	H	NHPh	−0.45	24	20	*f*
H	H	$N(Ph)_2$	−0.26	26	23	*f*
H	H	OMe	−0.20	27	25	*g*
H	H	Me	−0.14	28	25	*f*
H	H	H	0.00	29	26	*d*
H	H	Cl	+0.25	28	26	*f*
H	H	COMe	+0.56	28	26	*f*
H	H	CN	+0.68	28	26	*d*
H	H	NO_2	+0.77	28	26	*d*
Me	H	$N(Et)_2$	−0.72	22	17	*f*
Me	H	$N(Ph)_2$	−0.26	26	23	*f*
Me	H	Me	−0.14	29	26	*f*
Me	H	H	0.00	30	27	*f*
Me	H	NO_2	+0.77	29	26	*f*
Me	Me	$N(Et)_2$	−0.72	*h*	*h*	*h*
Me	Me	Me	−0.14	31	28	*f*
Me	Me	H	0.00	33	30	*f*
Me	Me	NO_2	+0.77	32	29	*f*

[a] Reference 4. [b] Estimated by extrapolation from Figure 3, see text. [c] Estimated from plot of log *k* vs. E_T in ref. 11. [d] Estimated from plot of log *k* vs. E_T. [e] Estimated from plot of log *k* vs. E_T in Figure 1. [f] Estimated by extrapolation from Figure 4, see text. [g] Estimated from plot of log *k* vs. E_T in Figure 2. [h] There are insufficient data to estimate accurately these values in Figure 4. This dye is reported in ref 19 to be a better quencher and presumably has a lower triplet energy than the corresponding dye minus the two methyl groups.

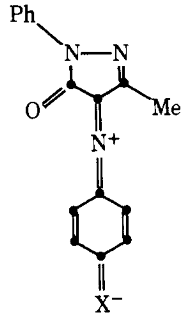
quench singlet oxygen more efficiently than the corresponding dye minus the two methyl groups.[19]



The breaks in the plots of Figures 3 and 4 show that azomethine dyes have higher triplet state energies when the substituent constants are near zero, but also that two different forces within the molecule are important in determining dye triplet energies. A dye whose triplet state energy is lowered by the presence of a strong electron-donating substituent should have a carbon–nitrogen double bond sufficiently weakened to permit isomerization by rotation. The transition state for this isomerization path is shown:



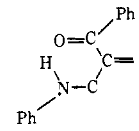
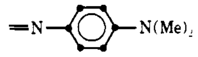
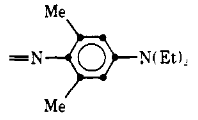
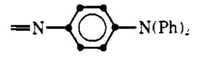
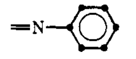
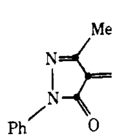
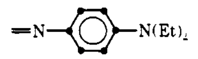
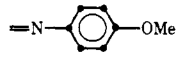
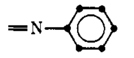
Electron-withdrawing substituents would be expected to interact with the remainder of the dye molecule in a manner different from the electron donors. Electron withdrawers should facilitate formation of the transition state for inversion as illustrated.



We are reminded of our investigation into the mechanism of the thermal isomerization of azomethine dyes where we concluded that these same substituents facilitate the isomerization reaction by the same two mechanisms described here.[4] A proposed relationship between the dye ground states and dye triplet states with regard to isomerization will now be presented.

Coming back to Figures 1 and 2, we shall now examine what happens in the plots in those regions where the rates of energy transfer have dropped below the diffusion-controlled level. One of the criteria frequently applied to this type of energy transfer plot is measurement of the limiting slope in the lower energy region. One might expect that any energy deficiency in the triplet sensitizer in providing energy to excite the dye to its triplet state would have to be made up thermally. Whether or not the Arrhenius equation is being followed can be determined from the final slope in the energy transfer plots, because the Arrhenius equation predicts a slope of 0.74 mol $kcal^{-1}$ at room temperature.[20] These slopes are, indeed, observed with such quenchers as biacetyl,[13] *trans*-stilbene,[21] and azulene.[22] With a number of other isomerizable systems, energy transfer in the lower energy regions proceeds more efficiently than predicted on the basis of this equation, and this behavior is revealed by slopes shallower than 0.74 mol $kcal^{-1}$ in the energy transfer plots. Previously, *cis*-stilbene,[21] *cis*- and *trans*-methylstilbene,[21] some aliphatic and aromatic azides,[23,24] and the isomers of some azastilbenes[25] all have demonstrated this

Table II. Data from Energy Transfer Measurements and Thermal Measurements Involving Azomethine Dyes

Dye		Final slope in energy transfer plot, mol kcal^{-1} [a]	Thermal barrier to syn–anti isomerization, kcal/mol [b]
		0.13	14
		0.13	12
		0.16	*d*
		0.17	*d*
		0.19	13
		*c*	13
		0.7	*d*
		0.4	*d*
		0.6	*d*
		0.7	15

[a] This column lists the values for the limiting slope in mol kcal^{-1} for the plots of log k vs. E_T. [b] This column lists the measured thermal barriers to isomerization from the less stable to the more stable dye isomer. These barriers were determined by measuring the isomer relaxation rates as a function of temperature and applying the Arrhenius equation. [c] There were no sensitizers with sufficiently low triplet energies available to carry out measurement of this number. [d] Not measured.

same behavior. This apparent deviation from the Arrhenius equation has been attributed to "nonvertical energy transfer" and involves excitation of the quenchers concomitant with a change in geometry that reduces the energy requirements in the quencher.[21,26-28] Many molecules that can isomerize about a double bond have minima in their triplet state potential energy surfaces for geometries intermediate between the isomers. The transition from one of the ground state isomers to the triplet minimum, although obscured spectroscopically, occurs during the energy transfer process, but at a rate that is less efficient than diffusion controlled. Since, through "nonvertical energy transfer", lower energy sensitizers transfer energy to the quenchers at a faster rate than would otherwise be expected, the final slopes of the energy transfer plots will be shallower than 0.74 mol kcal^1. We believe that the deviation of the slopes from the Arrhenius equation slope in energy transfer plots can be taken as a measure of "nonvertical energy transfer" to the overall energy transfer process. For shallow wells in the triplet potential energy surface, the amount of energy gained for the "nonvertical energy transfer" process is small, and the slopes in the plots should be only a little smaller than 0.74 mol kcal^{-1}. With deep wells in the triplet state potential energy surfaces, by contrast, "nonvertical energy transfer" should become more important with lower energy sensitizers and shallower slopes should obtain in the energy transfer plots.

For those dyes under consideration here where complete energy transfer plots were constructed, Table II lists the limiting slopes of these plots. Since all slopes for the various benzoylacetanilide azomethine dyes are substantially less than 0.74 mol kcal^{-1}, we believe that "nonvertical energy transfer" occurs with these dyes, but that the extent of its contribution varies. As the substituents shift from electron donating to electron withdrawing in character, the limiting slopes in their respective energy transfer plots increase somewhat in value. These changes in slope, however, are not sufficiently large to negate our assignments of dye triplet energies based on the data plotted in Figure 3 (vide supra). So far as the pyrazolone azomethine dyes are concerned, the measured slopes are not well defined because the plots could not be expanded due to a scarcity of satisfactory low energy sensitizers. These pyrazolone dye slopes show no apparent trend as the nature of the substituents change, but experimental error may obscure any existing trend. If we had better means of measurement, we might find some of these slopes to be identical with the 0.74 mol kcal^{-1} standard. At any rate, there can be little doubt that the limiting slopes in the energy transfer plots for the benzoylacetanilide dyes are smaller than those for the pyrazolone azomethine dyes.

The foregoing results indicate that the azomethine dyes investigated here also fall into that class of molecules with isomerizable double bonds that have triplet state potential energy surfaces with minima at geometries between the two isomers. In order to map out with some degree of accuracy the potential energy surfaces of the dye ground states and triplet states as a function of dye geometry, additional data are required. One should have a measure of the thermal barriers between the two dye isomers. Such data are available for some of the dyes from measuring as a function of temperature the rates of relaxation of the less stable dye isomer to the preferred dye configuration followed by application of the Arrhenius equation. Results are included in Table II. Since the thermal barrier measurements are for the isomerization in one direction only, they do not reveal the size of the barrier for isomerization of the preferred configuration to the less stable isomer. These barriers, however, can be estimated if one had some idea of the energy differences between the preferred and the less stable isomers. Although these differences have not been measured directly, it is possible, from NMR data to estimate a minimum energy difference between the two isomers. One can determine by NMR spectroscopy whether both isomers are present in solution simultaneously. For the dyes considered here, one dye isomer seems to overwhelm the isomeric equilibrium. If one estimates that as little as 1% of the less stable dye isomer would be detectable were it present, the equation relating the free energy change to the equilibrium constant can be applied to estimate a minimum ground state energy difference between the isomers. The value for this minimum difference is close to 3 kcal/mol. Adding the 3 kcal/mol energy value to the measured thermal barriers of Table II yields minimum values for the thermal barriers to isomerization from the preferred to the less stable isomers.

Armed with all the foregoing data, we shall now begin to construct our model for the photochemical isomerization of these dyes. The triplet and ground state potential energy surfaces are interrelated and together provide a path for the dye isomerization. The information we have concerning the ground state potential energy surfaces will aid in mapping out the triplet state potential energy surfaces. The potential energy surfaces for the ground and triplet states are almost like mirror images in the sense that the maximum in the ground state between the two geometric isomers coincides

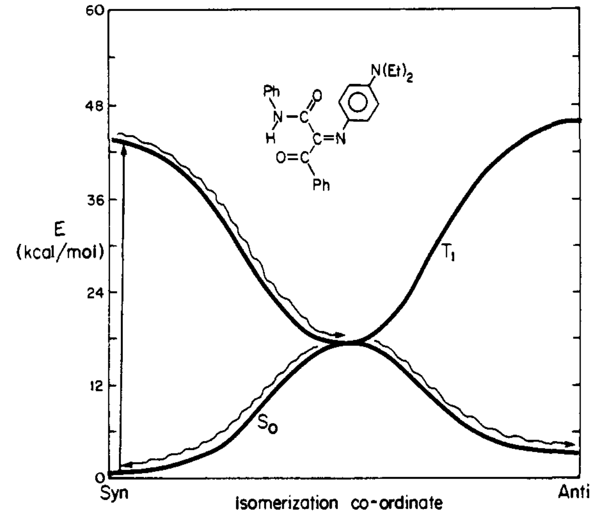


Figure 5. Proposed ground state and triplet state potential energy surfaces for a benzoylacetanilide azomethine dye substituted with an electron-donating substituent and plotted as a function of the isomerization coordinate. The solid and wavy arrows represent the energy transfer and subsequent radiationless deactivation steps resulting in the isomerization reaction.

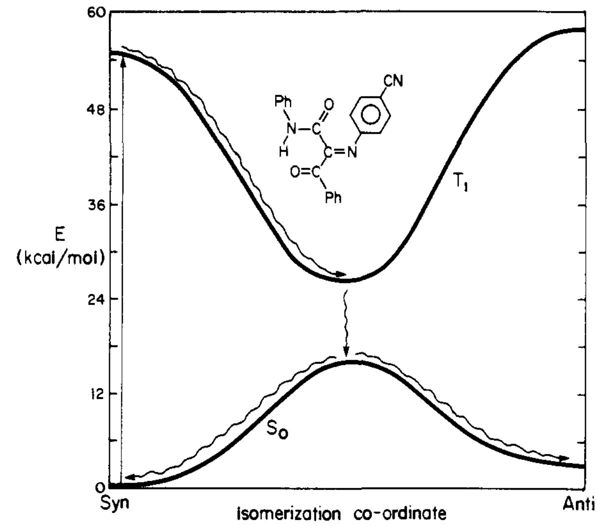


Figure 6. Proposed ground state and triplet state potential energy surfaces for a benzoylacetanilide azomethine dye substituted with an electron-withdrawing substituent and plotted as a function of the isomerization coordinate. The solid and wavy arrows represent the energy transfer and subsequent radiationless deactivation steps resulting in the isomerization reaction.

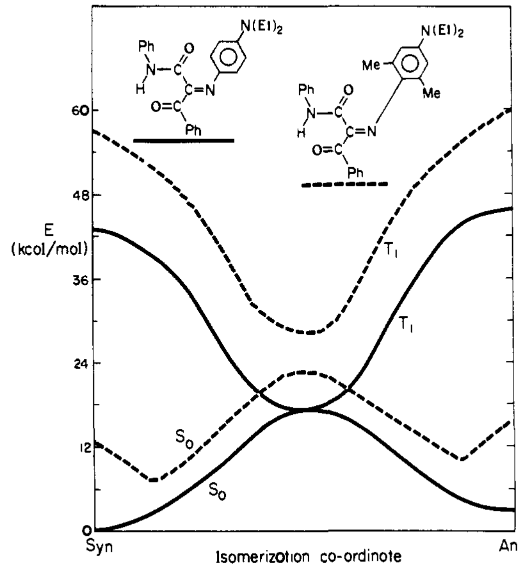


Figure 7. Proposed changes as a function of the isomerization coordinate in the ground state and triplet state potential energy surfaces of the illustrated azomethine dyes brought about by introduction of two methyl groups to provide steric hindrance about the C=N bond.

with the minimum in the triplet state. The simplest manner to describe these interrelated potential energy surfaces in detail is to illustrate them and this is done in Figures 5-9.

Beginning with Figure 5, this shows the proposed potential energy surfaces for a benzoylacetanilide dye with a strong electron-donating substituent in the para position of the aromatic ring attached to the azomethine nitrogen atom. The isomerization coordinate plotted along the abscissa for the dyes is the angle of twist about the C=N bond. We know from the measured slopes of Table II that the wells in the triplet state potential energy surfaces are deep and, because energy transfer still is measurable with our lowest energy sensitizers, suspect that they are so deep that in the twisted dye configuration the triplet minimum meets the ground state maximum. The photochemical triplet isomerization would then proceed as illustrated by the paths first of the solid and then by the wavy arrows. Energy transfer from an appropriate sensitizer leads to excitation of the dye from its preferred ground state geometry to the lowest triplet state followed by rapid relaxation with concomitant twisting to the triplet potential minimum; at this point intersystem crossing to the ground state occurs and the dye molecules are partitioned between the two isomers. The less stable isomer, however, cannot be isolated at room temperature and will thermally revert back to the initial configuration.

Figure 6 illustrates the situation for a benzoylacetanilide azomethine dye substituted with an electron-withdrawing substituent. Here the isomerization coordinate along the abscissa represents the degree of inversion. From the data of Table II, we do not believe that the triplet minimum is as deep as in Figure 5 and do not show it coming into contact with the ground state. Isomerization would proceed by a similar route as outlined with reference to Figure 5.

In Figure 7 an attempt is made to account for steric effects in the isomerization process. The two dyes selected for comparison here are illustrated. The solid lines show the ground state and triplet state potential energy surfaces for the dye without the two methyl groups, and the dotted lines show the proposed changes that these two methyl groups bring about.

In the case of the pyrazolone azomethine dyes, the situation with regard to the triplet potential energy surfaces has changed in that shallow wells rather than deep wells are present. This is required by the low dye triplet energies of Table I and the relatively steep slopes and moderately large thermal barriers of Table II. Figures 8 and 9 show the proposed potential energy surfaces for pyrazolone dyes substituted with an electron donor and an electron withdrawer, respectively. In the former figure, the isomerization coordinate is the angle of twist and in the latter figure the degree of inversion, both about the C=N bond.

Experimental Section

Materials. The dyes were synthesized by oxidative coupling of either benzoylacetanilide or 3-methyl-1-phenyl-2-pyrazolin-5-one with the appropriately substituted *p*-phenylenediamine, potassium ferricyanide being used as the oxidizing agent, or by condensation of 1-phenyl-3-(*N*-phenylamino)propanetrione or 3-methyl-1-phenyl-2-pyrazoline-4,5-dione with the appropriately substituted aniline, using boron trifluoride as catalyst.[29]

The sources and purification procedures for the triplet sensitizers are given elsewhere.[11,12] The benzene was Mallinckrodt Nanograde and was used as received.

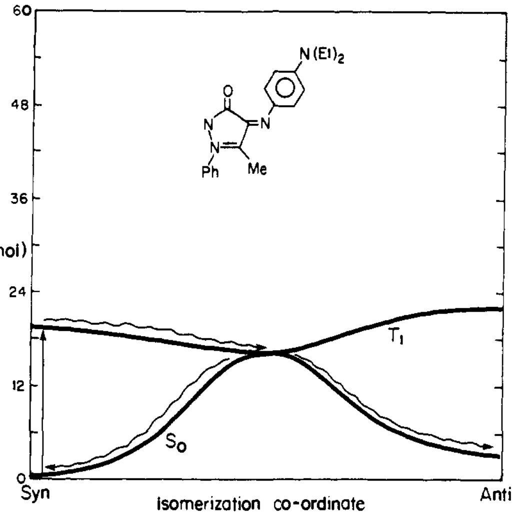


Figure 8. Proposed ground state and triplet state potential energy surfaces for a pyrazolone azomethine dye substituted with an electron-donating substituent and plotted as a function of the isomerization coordinate. The solid and wavy arrows represent the energy transfer and subsequent radiationless deactivation steps resulting in the isomerization reaction.

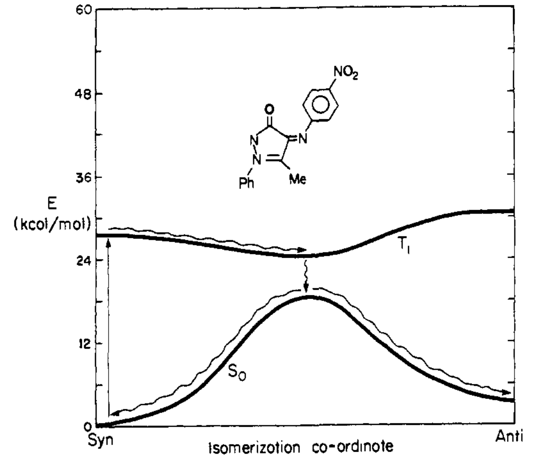


Figure 9. Proposed ground state and triplet state potential energy surfaces for a pyrazolone azomethine dye substituted with an electron-withdrawing substituent and plotted as a function of the isomerization coordinate. The solid and wavy arrows represent the energy transfer and subsequent radiationless deactivation steps resulting in the isomerization reaction.

Procedures. Kinetic measurements were carried out on a conventional flash photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H20) were positioned on opposite sides of an 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 a 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.[30,31]

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(14) 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 due to the escape of either the triplet sensitizer or the quencher from the solvent cage prior to reaction.[15–17]
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(20) 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 equation, one obtains

$$\Delta \log k = -\Delta E_a/(2.3RT)$$

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 $\Delta \log k$ 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 $\log k$, respectively.
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