Quenching of Singlet Molecular Oxygen in Solution by Azomethine Dyes[1]

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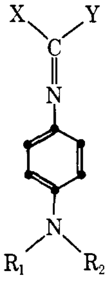
Abstract: Azomethine dyes are ineffective as photosensitizers for singlet oxygen but instead constitute a new class of solution quenchers for this species. Quenching of the photooxygenation of 2-methylpentene-2 was used to determine $^1O_2$ quenching efficiencies for several of these dyes in C_5H_5N, C_6H_6, and CH_3CN. There is a trend toward increased quenching efficiency as the wavelength of maximum absorption of the dye shifts bathochromically. Stèric crowding ortho to the azomethine linkage generally results in a bathochromic shift and increased quenching efficiency, whereas steric crowding ortho to the dialkylamino group in the developer moiety may result in a hypsochromic shift and decreased quenching efficiency. The amino group in the developer moiety is apparently necessary, but not sufficient, for high $^1O_2$ quenching efficiency. A mechanism is proposed for the $^1O_2$ quenching reaction involving the formation of a dye–$^1O_2$ excited complex, the binding energy of which is increased by energy-transfer and charge-transfer contributions.

Of the compounds known to quench singlet molecular oxygen ($^1O_2$) in solution, carotenoids[2-4] and amines[5-11] have been investigated most extensively. The available evidence indicates that carotenoids quench by a spin-allowed energy-transfer mechanism, whereas amines quench by a charge transfer (CT) mechanism. Normally dyes are not associated with quenching of $^1O_2$ but rather with the sensitized formation of this species.[12-14] We have found a class of dyes, however, whose members are quenchers, rather than photosensitizers, for $^1O_2$. These are the azomethine dyes.

To the extent that quenching of $^1O_2$ by a dye may occur by an energy-transfer process, then a "dye" that absorbs in the infrared region of the spectrum would be a good candidate as a quencher. Recently Merkel and Kearns,[15] for example, showed that a polymethene pyrylium dye with optical absorption in the region of 1.1 μ quenched $^1O_2$ at the diffusion-controlled rate ($k_q = 3 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$) in acetonitrile. Azomethine dyes do not require absorption in the infrared region in order to quench. In fact, we have found quenching of $^1O_2$ by some blue-absorbing azomethine dyes, albeit at less than the diffusion-controlled rate.

The general structure of azomethine dyes is shown in **1**.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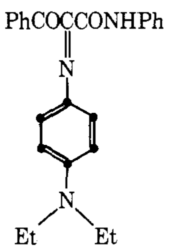
They may be prepared (cf. Experimental Section) either by oxidative coupling of an appropriate "coupler" (X-CH_2-Y, wherein -CH_2- is an active methylene group) with a *p*-phenylenediamine, or by condensation of an appropriate keto-coupler (X-C(=O)-Y) with a *p*-phenylenediamine. X and Y may be part of the same ring. Typical examples of azomethine dyes that absorb in the blue, green, and red regions of the spectrum are shown in **2–4,** respectively. Such dyes are examples of the yellow, magenta, and cyan image dyes used in the subtractive color photographic process.[16] Generally the coupler moiety is more important than the *p*-phenylenediamine in determining the spectral region in which these dyes absorb. An exception to this is the ortho,ortho′-disubstituted *p*-phenylenediamines (**5**), which give bathochromically shifted dyes, particularly with pyrazolone couplers.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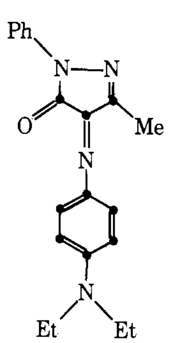
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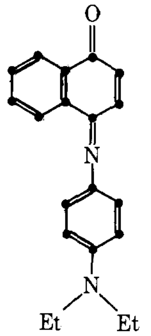
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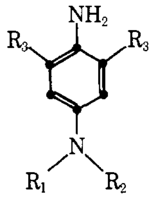
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Azomethine dyes (**1**) could be viewed as para-substituted anilines, and as such would be expected to quench $^1O_2$. Young et al.[9] have shown that quenching rate constants for a series of para-substituted *N,N*-dimethylanilines correlate reasonably well with σ^- substituent constants. However, azomethine dyes are better quenchers than would be predicted on the assumption that they are simply para-substituted anilines.

Using flash techniques, we have measured rate constants for triplet energy transfer from several low-energy sensitizers to azomethine dyes. These experiments were carried out to determine the importance of energy transfer vs. charge transfer in the quenching of $^1O_2$ by azomethine dyes.

Experimental Section

Materials. A typical preparation of an azomethine dye (**10A**; cf. Table I) by an oxidative coupling reaction is as follows. In the minimum amount of ethyl alcohol (ca. 200 ml) was dissolved 4.32 g (0.02 mol) of 1-phenyl-3-*tert*-butyl-2-pyrazolin-5-one. This solution was placed into an erlenmeyer flask equipped with a magnetic stirrer. The following solutions were then added in succession with

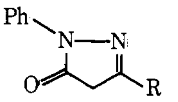
Table I. Couplers and Developers

Couplers

$RCOCH_2CONHPh$

7, R = Ph

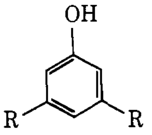
8, R = *t*-Bu



9, R = Me

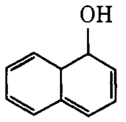
10, R = *t*-Bu

11, R = PhCONH



12, R = H

13, R = Me



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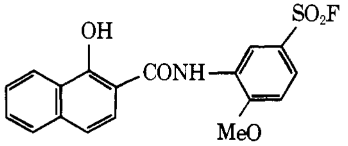

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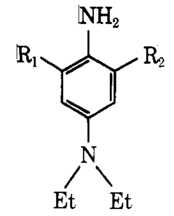
Developers



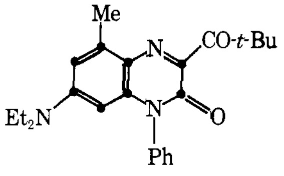
A, $R_1 = R_2 = H$

B, $R_1 = H$; $R_2 = Me$

C, $R_1 = R_2 = Me$

stirring: 20 g (0.2 mol) of Na_2CO_3 in 600 ml of H_2O; 4.0 g (0.02 mol) of *N,N*-diethyl-*p*-phenylenediamine hydrochloride in 400 ml of H_2O; and finally 500 ml of H_2O to facilitate precipitation of the dye. If the addition of the Na_2CO_3 solution precipitated the coupler, additional ethyl alcohol was added. The dye was filtered (extracted with CH_2Cl_2 if an oil), dried, and purified.

Either one of two sensitizers for $^1O_2$ was used in this study, Rose Bengal or azine **6**. The former was useful for polar solutions, the latter for nonpolar solutions. Rose Bengal was Eastman reagent grade, 84% dye content, used without purification. The azine was prepared as follows. Pivaloylacetanilide [8.8 g (0.04 mol)] was dissolved in 800 ml of ethyl alcohol. The following solutions were then added in succession with stirring: 500 ml of aqueous NaOH (pH 12); 8.6 g (0.04 mol) of 4-amino-3-methyl-*N,N*-diethylaniline hydrochloride in 100 ml of H_2O; and 40 g (0.12 mol) of $K_3Fe(CN)_6$ in 300 ml of H_2O. The precipitated dye was filtered, dried, and purified by chromatography over silica gel to mp 162–163°.



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Pyridine and acetonitrile were Eastman reagent grade, used without further purification. Benzene was Mallinckrodt Nanograde, also used without further purification. 2-Methylpentene-2 was Phillips Petroleum Co. pure grade, 99 mol % minimum. This was passed over a short column of aluminum oxide (Woelm neutral) prior to use.

Kinetic Method for Measuring Quenching Efficiencies. The kinetic method that was used has been described by Foote and Denny[2] and consequently is only briefly outlined here. Their technique permits separation of the quenching efficiency of $^1O_2$ by a quencher both from the quenching of sensitizer triplet and from any apparent quenching due to light absorption by the quencher. The following scheme adequately describes the reactions involved:

$$\text{Sens}\ (S_0) \xrightarrow{h\nu} \text{Sens}\ (S_1) \longrightarrow \text{Sens}\ (T_1)$$

$$\text{Sens}\ (T_1) + O_2 \longrightarrow \text{Sens}\ (S_0) + {}^1O_2$$

$${}^1O_2 \xrightarrow{k_d} O_2$$

$${}^1O_2 + A \xrightarrow{k_A} AO_2$$

$${}^1O_2 + Q \xrightarrow{k_q} O_2 + Q$$

The inverse rate of oxygen absorption is given by the expression[2] in eq 1, where (A) is the concentration of the $^1O_2$ acceptor, (Q) is the

$$\text{rate}^{-1} = C\left[1 + \frac{k_d + k_q(Q)}{k_A}\,\frac{1}{(A)}\right] \qquad (1)$$

concentration of the $^1O_2$ quencher, and C is a term whose value depends upon the triplet yield of the sensitizer, the yield of $^1O_2$, and the fraction of light absorbed by the sensitizer. From a plot of rate^{-1} vs. $(A)^{-1}$ at constant (Q), the ratio of slope/intercept gives either k_d/k_A (known as "β")[17] when (Q) = 0 or $\beta[1 + k_q\tau(Q)]$ when $(Q) \neq 0$. From the latter, the quenching efficiency of the quencher, $k_q\tau$ ($\equiv k_q/k_d$), is easily calculated. Since (A) is varied, while (Q) is held constant, the ratio of slope/intercept does not depend upon whether Q quenches or reacts with the triplet state of the sensitizer. No evidence was found for chemical reaction of any of the azomethine dyes with $^1O_2$ during the kinetic runs. Using chemical sources of $^1O_2$, we estimate the chemical yield of dye destruction by $^1O_2$ to be <0.1%.[18]

Apparatus for Measuring Quenching Efficiencies. The reactions were followed by measuring the rate of oxygen consumption in a constant-pressure, automatic recording gasometer apparatus. This apparatus is basically a hybrid of two that are described in the literature.[19,20] The absorption cell was similar to the one described by Mahoney et al.,[19] and the physical arrangement of the gasometer itself was similar to that of Traylor and Russell.[20] Pressure differentials were detected by a Schaevitz P476-A10 pressure transducer (0–10 in. of water), which was attached to the gasometer via small-diameter, stainless-steel tubing with Swagelok fittings. The signal from the transducer activated a Harvard infusion-withdrawal pump. This pumped mercury into a gas buret attached to the gasometer until the null point of the transducer was reached. The pump displacement was converted to a voltage change by appropriate gearing of the pump to a Helipot linear potentiometer. Output from the potentiometer was fed into a 10-mV span strip chart recorder, equipped with chart speeds of 2, 5, 8, and 20 in./hr (Varian Associates Model G11A). Rates as low as 10^{-7} M sec^{-1} can be measured on a 10-ml sample.

Flash-Photolysis Experiments. Kinetic measurements were carried out on a flash-photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H20) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inner walls were coated with reflective paint (Eastman white reflectance coating). The energy of the flash discharge was 400 J and 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 dc power supply (Sorensen QSB12-8). The lamp was mounted in a housing on an optical bench together with the flash chamber and a 0.25-m monochromator (Jarrell-Ash). The monitoring beam was collimated and, 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) mounted on the exit slit of the monochromator. The electrical signal from the photomultiplier was fed into a cathode-follower amplifier and then fed into a wide-band oscilloscope (Tektronix 555). Oscillographs were photographed by 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 round-bottomed bulbs where the solutions were contained while being degassed. Solutions were degassed on a high-vacuum manifold, and the sample containers were sealed after several freeze-pump-thaw cycles.

The oscillographs were enlarged to facilitate more precise measurement of the transient phenomena. The lifetime of a transient species was measured by the recovery rate of the monitoring beam

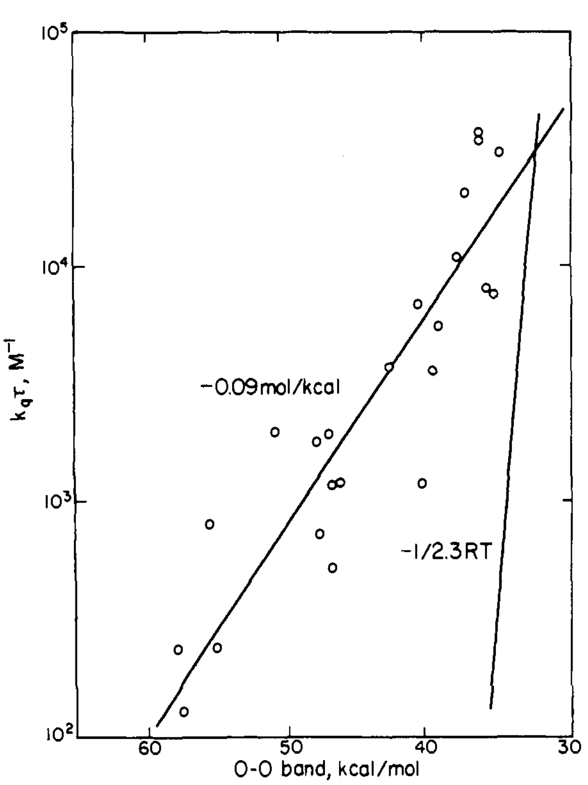


Figure 1. Dependence of quenching efficiency on the 0-0 absorption band of the dye; pyridine solution.

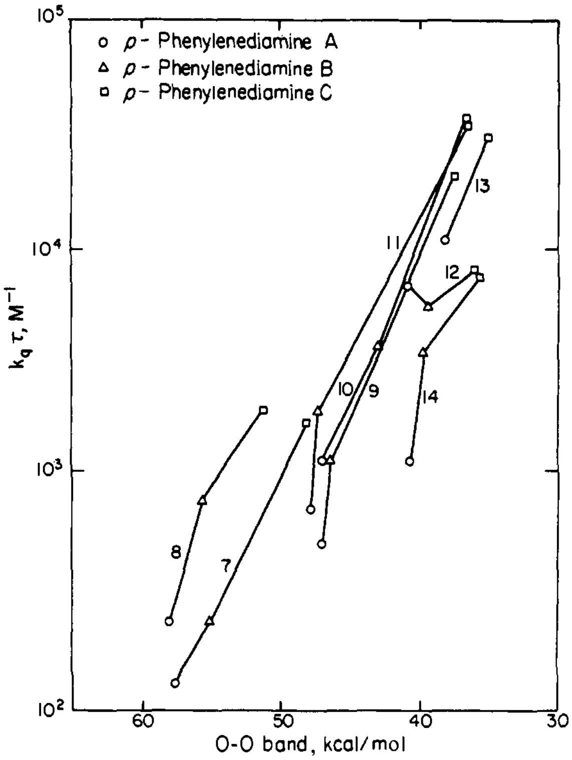


Figure 2. Dependence of quenching efficiency on the 0-0 absorption band of the dye; pyridine solution. Arabic numerals refer to coupler structure (Table I).

after the excitation flash. Kinetic analysis was by the method of Linschitz and Sarkanen.[21]

Sensitizer Triplet Energies. The triplet energy level of azine **6**, which was used as a singlet-oxygen sensitizer, was determined from its phosphorescence spectrum to be 46 kcal/mol. The measurement was made with a conventional spectrophosphorimeter with a slotted, rotating can to separate phosphorescence from total luminescence. The dye was dissolved in a 6:1 mixture (by volume) of methylcyclohexane and 3-methylpentane,[22] and the glass-forming solution was placed in a quartz tube submerged in liquid nitrogen, under which conditions, the measurements were carried out.

The value for E_T for triplet violanthrene was estimated from eq 2, where Δm is the calculated Hückel molecular orbital (HMO) transition energy, in β units, of the sensitizer. Equation 2 was ob-

$$E_T(\text{kcal/mol}) = 0.710\ (\pm\ 6.34) + 52.24\ (\pm\ 11.00)\Delta m \qquad (2)$$

tained by plotting E_T values against Δm values for six alternate hydrocarbons, all of whose triplet energies lie below 40 kcal/mol. In the case of the two sensitizers of lowest triplet energy (pentacene, 23.0 kcal/mol and pyranthrene, 26.9 kcal/mol), experimental values of E_T were unavailable, and therefore values from molecular orbital calculations more refined than the HMO method were used.[23,24] The equation of this line is subject to considerable error, as is evidenced by the standard deviations of the slope and intercept. The standard deviation of a single E_T value is ±2.1 kcal/mol, and the 95% confidence limit, ±5.4 kcal/mol. Substitution of the calculated HMO transition energy for violanthrene, 0.47 β, into eq 2 gives $E_T = 25 \pm 2$ kcal/mol.

Results

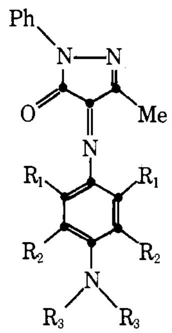
Singlet-Oxygen Quenching Efficiencies. Using either Rose Bengal or azine **6** as sensitizer, the $^1O_2$ quenching efficiencies of several azomethine dyes were measured in pyridine, benzene, and acetonitrile solution by quenching of the reaction of $^1O_2$ with 2-methylpentene-2. The β values for the olefin were measured in each solvent using the kinetic method of Foote and Denny[2] and found to be 0.043 (pyridine), 0.053 (benzene), and 0.018 *M* (acetonitrile). These values were used to calculate $k_q\tau$ values for the dyes (cf. Experimental Section). The results for pyridine solution are plotted in Figure 1 as a function of the 0-0 absorption band of the dye, the latter being estimated by extrapolation of the long-wavelength side of the absorption band of each dye to zero absorbance. For these dyes, the lower the energy of the 0-0 band, the better the dye is as a $^1O_2$ quencher, although this is not without exceptions. The dyes for which $k_q\tau$ values are plotted in Figure 1 were derived from eight couplers and three *p*-phenylenediamines, the structures of which are shown in Table I. (Dyes **2-4**, cited above as examples of azomethine dyes, are the same as dyes **7**A, **9**A, and **14**A in Table I, respectively.)

Figure 2 is a plot of the same data as Figure 1, but dyes derived from the same coupler are indicated.[25] With a fixed coupler, the order of efficiency is A < B < C (except with coupler **12**). Increasing alkyl substituents ortho to the azomethine linkage enhances quenching efficiencies; the 0-0 absorption band shifts bathochromically in the same order.

While alkyl substituents ortho to the azomethine linkage usually increase the efficiency of the dye for quenching $^1O_2$, alkyl substituents ortho to the dialkylamino group have the opposite effect. For example, comparison of the quenching rate constants[26] in acetonitrile of **9**A vs. **22** and **9**C vs. **23** shows that dimethyl substitution ortho to the dialkylamino group results in diminution of log k_q by two to three orders of magnitude. The case of dyes **9**A and **22** is one in which the empirical correlation of Figure 1 does not hold; the two dyes have similar λ_{max} and 0-0 absorption (**9**A, 607 nm; **22**, 630 nm) yet differ in quenching efficiencies by two or more orders of magnitude (Chart I).

When the amino group in the *p*-phenylenediamine moiety is unsubstituted, dialkyl substitution ortho to this nitrogen does not introduce enough steric hindrance to even null the rate enhancement due to dialkyl substitution ortho to the azomethine bond. Thus, the tetramethyl dye **24** is about a tenfold better quencher than the analogous unsubstituted dye **16** (Chart II).

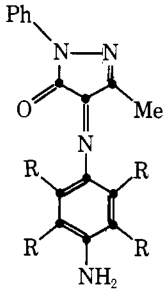
Chart I



	R_1	R_2	R_3	log k_q[a] (CH_3CN)	λ_{max}, nm (CH_3CN)
9A	H	H	Et	8.6	520
22	H	Me	Me	6.8	518
9C	Me	H	Et	9.6	640
23	Me	Me	Me	6.6	551

[a] Cf. ref 26.

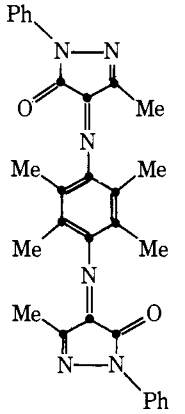
Chart II



	R	log k_q[a] (CH_3CN)	λ_{max}, nm (CH_3CN)
16	H	7.7	480
24	Me	8.7	615

[a] Cf. ref 26.

The presence of the aromatic amino group is apparently important for $^1O_2$ quenching efficiency, as exemplified by compounds **25** and **26**. No measurable quenching of $^1O_2$ was found with either compound at a concentration of 2×10^{-3} *M*, although both compounds quench triplet violanthrene ($E_t \simeq 25$ kcal/mol) in benzene at near the diffusion-controlled rate (**25**, 2.5×10^9 M^{-1} sec^{-1}; **26**, 1.7×10^9 M^{-1} sec^{-1}) (Table II).



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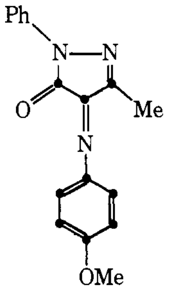

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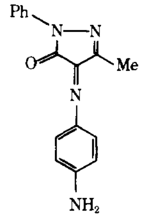
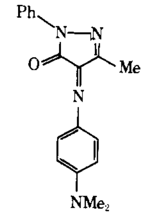
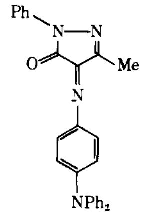
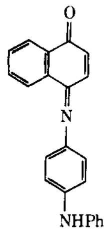
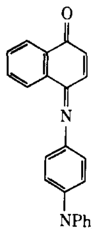
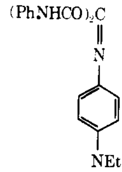
In Table III, we show the effect which both the concentration of oxygen and the nature of the solvent have upon the quenching rate constants. It was found that increasing

Table II. Comparison of Rate Constants for Quenching of Triplet Violanthrene and Singlet Oxygen by Azomethine Dyes

Dye	λ_{max},[a] nm	Log k_q[c] ^{3}Viol[b]	Log k_q[c] $^1O_2$[a]
9C	641	9.5	8.8
10C	647	(9.5)[d]	9.0
11C	650	(9.5)[d]	9.0
13C	675	9.5	9.0
15C	768	9.6	9.2
7A	433	6.8[e]	6.6[e]
7B	446	7.2[f]	6.9
7C	477	6.9	7.8
8A	428	6.6	6.9
8B	440	6.7	7.4
9A	520	9.5	7.6
9B	534	9.3	7.6
(16) 	495	9.5	7.7[g]
(17) 	519	9.5	7.6
(18) 	537	9.4	7.7[g]
(19) 	571	9.3[h]	<7.6
(20) 	562	9.1[h]	<6.5
(21) 	435	8.9	7.2

[a] Pyridine solution. [b] Benzene solution. [c] Units of *k*: M^{-1} sec^{-1}. [d] Assumed value, based upon rate constant for dye of very similar structure. [e] Datum is actually for the *N,N*-dimethyl dye. [f] Extrapolated from data using sensitizers with slightly higher E_T. [g] Acetonitrile solution; value for pyridine solution would be lower. [h] Value given is for zinc phthalocyanine (E_T = 26 kcal/mol).[39]

Table III. Rate Constants for Quenching of Singlet Oxygen by Azomethine Dyes in Air- and Oxygen-Saturated Solvents

	k_q, M^{-1} sec^{-1} × 10^9		
Dye	C_6H_6	C_5H_5N	CH_3CN
15C	6.0 (a)[a]	1.5 (a)	39 (a)
	3.4 (o)	1.2 (o)	
9C	0.67 (a)	0.65 (a)	3.8 (a)
	1.5 (o)	0.57 (o)	
10B	0.17 (a)	0.12 (a)	1.3 (a)
	0.082 (o)	0.19 (o)	
9A	0.010 (a)	0.016 (a)	0.41 (a)
	0.014 (o)	0.018 (o)	

[a] (a) = air saturated; (o) = oxygen saturated.

the oxygen concentration about fivefold (i.e., air- vs. oxygen-saturated solution) had no systematic effect upon the quenching rate constants in either solvent for any of four dyes (Table III, columns 2 and 3). Note that the four dyes selected have $^{1}O_2$ quenching efficiencies which span approximately two orders of magnitude.

Quenching rate constants are approximately tenfold greater in acetonitrile solution than in either benzene or pyridine. The quenching rate constant for dye **15C** in acetonitrile (3.9 × 10^{10} M^{-1} sec^{-1}) indicates that quenching is diffusion controlled. In pyridine, however, the quenching rate constant for the same dye is approximately fourfold below the value calculated for k_{diff} (2 × 10^{10} M^{-1} sec^{-1}) using the Debye equation[28] and making allowance for the relatively large diffusion coefficient for oxygen.[29,30]

Triplet Energy-Transfer Experiments. Using flash methods, we measured rate constants for energy transfer from a low-energy triplet sensitizer, violanthrene ($E_T \simeq 25$ kcal/mol), to the dye quenchers of $^{1}O_2$ in benzene solution.[31] It was found that those dyes that quenched $^{1}O_2$ most efficiently (red- and infrared-absorbing dyes) were also the best quenchers of violanthrene triplets (Table II, first set of data), and that those dyes that were the poorest quenchers of $^{1}O_2$ (blue-absorbing dyes) were also inefficient quenchers of violanthrene triplets (Table II, second set of data). With azomethine dyes which absorb light principally in the green region of the spectrum, however, quenching efficiencies toward the two quenchees often differed by approximately two orders of magnitude, those for $^{1}O_2$ being the lesser (Table II, third set of data).

In the above experiments, the quencher (azomethine dye) was varied, while the sensitizer (violanthrene) was held constant. We also measured rates of energy transfer for cases in which the quencher (azomethine dye) was held constant, while the sensitizer (hydrocarbon) was varied. An example is shown in Figure 3, where the logarithms of the rate constants for triplet energy transfer (degassed benzene) from a series of sensitizers to a representative yellow dye, **8B**, are plotted as a function of the triplet energy of the sensitizers.[23,32,33] The slope of this line is 0.11 mol/kcal. The average slope for 13 yellow dyes was 0.20 ± 0.16 mol/kcal.

Discussion

Sensitizing Inefficiency of Azomethine Dyes. Before discussing the mechanism for quenching $^{1}O_2$ by azomethine dyes, a point should be made about their inefficiency as sensitizers for $^{1}O_2$ formation. This inefficiency may result from low triplet yields, short triplet lifetimes, or both. Flexibility about the C=N bond probably provides a facile path for radiationless decay of an excited state of these dyes, leading to short lifetimes. Others[34-36] have proposed that rotation about the C=N bond in azomethines may be an important path for dissipation of electronic excitation energy. Furthermore, it is known that syn-anti isomerism is a major route for deactivation of azomethine dyes[37] and oxime *O*-methyl ethers.[38,39] In benzene solution, isomerization quantum yields are insensitive to the presence of dissolved air.[40]

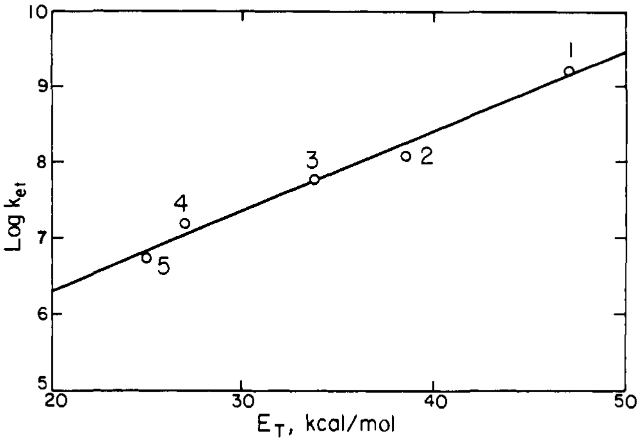
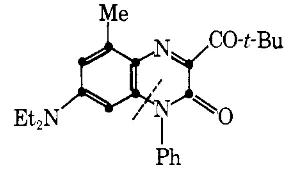


Figure 3. Rates of triplet energy transfer in benzene solution from selected sensitizers to dye **8B**. Sensitizers: (1) benzanthrone (E_T = 47.0 kcal/mol);[32] (2) 5-methyl-3,4,9,10-dibenzopyrene (38.5);[33] (3) anthanthrene (33.8);[33] (4) pyranthrene (**27**, MO calculations);[23] (5) violanthrene (**25**, HMO calculations).

In this connection, it is interesting to compare the $^{1}O_2$ sensitizing and quenching efficiencies of azomethine dye **8B** with azine dye **6**. The latter differs from the former by the presence of a bond from the amide nitrogen to the aromatic ring of the developer. This bond prevents rotation about the C=N bond. As a result, the azine is a sensitizer, whereas dye **8B** is a quencher, for $^{1}O_2$. Furthermore, the azine has a triplet lifetime of 80 μsec in degassed benzene at 22°, but we are unable to detect the triplet not only of **8B** but of any azomethine dye by either sensitized or unsensitized flash experiments under the same conditions. Consequently, the lifetime of azomethine dye triplet states is less than the lower limit of detection of transients on our flash apparatus, namely 10 μsec.



6 (Ar-N bond present)
8B (Ar-N bond absent)

$^{1}O_2$ Quenching Mechanism for Azomethine Dyes. The empirical correlations of Figures 1 and 2 could result from a systematic relationship between either triplet energies or ionization potentials of the dyes and their respective 0-0 absorption. If energy transfer is invoked to explain the correlation of Figures 1 and 2, then yellow dyes are orders of magnitude better quenchers of $^{1}O_2$ than would be predicted on the basis of the Arrhenius equation.[32] Equating the endothermicity of an energy-transfer step to the activation energy for this step leads to a prediction for the slopes of Figures 1 and 2 of $-1/2.3RT$ or -0.73 mol/kcal at 25°. The observed slope is only -0.09 mol/kcal. Here we have a case of variable quencher with constant quenchee ($^{1}O_2$), but shallow slopes were also obtained for rates of triplet energy transfer from a series of sensitizers to a constant azomethine dye. An example of the latter is shown in Figure 3. Thus, $^{1}O_2$ and triplet violanthrene do behave similarly in that both are quenched with unexpectedly high efficiency by yellow azomethine dyes.[41]

This result is reminiscent of that reported for rates of energy transfer from variable sensitizers to certain olefins, namely *cis*-stilbene and *cis*- and *trans*-1,2-diphenylpropene.[32] With these substrates, rates of energy transfer from triplet sensitizers are higher than expected when the triplet excitation energy of the sensitizers is insufficient to produce any known vertical transitions in the olefins. The results have been explained as due to nonvertical energy transfer, the olefin twisting about the C=C bond concomitant with energy transfer. The shallow slopes of Figures 1, 2, and 3 may result from a similar phenomenon, the dyes rotating about the C=N bond during the energy-transfer step.

Magenta dyes quench ${}^1O_2$ with efficiencies that are two or more orders of magnitude less than those for quenching triplet violanthrene (Table II). This dichotomy is not easily rationalized on the basis of an energy-transfer mechanism for ${}^1O_2$ quenching. If we adopt the hypothesis that quenching of ${}^1O_2$ and triplet violanthrene are both energy-transfer processes, then two rationalizations for this dichotomy should be considered. Based upon the existing data, neither of these is satisfactory.

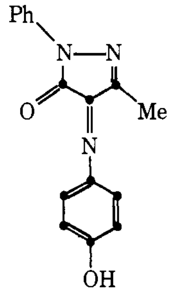
The first is that the difference in quenching efficiencies simply reflects the difference between the energies of triplet violanthrene (~25 kcal/mol) and ${}^1O_2$ (22.5 kcal/mol). This difference is sufficient to given an approximately 100-fold difference in quenching efficiencies provided (a) the vertical triplet energies of magenta dyes are no less than 25 kcal/mol, and (b) with sensitizers below 25 kcal/mol, the endothermicity of the energy-transfer step is equivalent to the activation energy for the same step. The latter assumption implies that rotation about the C=N bond does not occur in the triplet manifold for these dyes, or that there is an activation energy for this process. Based upon our results with yellow azomethine dyes, assumption b seems unlikely. Unfortunately, we are unable to test a for magenta (or cyan) dyes, because rates of energy transfer are still diffusion controlled with our lowest energy sensitizers.

A second possibility for an inefficiency in rates of energy transfer from ${}^1O_2$ to magenta azomethine dyes is that reversible energy transfer is occurring (eq 3). In air-saturated

$$ {}^1O_2 + \text{dye} \rightleftharpoons {}^3O_2 + {}^3\text{dye} \qquad (3) $$

pyridine, the oxygen concentration (~10^{-3} *M*) is 10-25 times greater than the violanthrene concentrations used in degassed benzene in the flash experiments. Other things being equal, reversible energy transfer would be more likely in the ${}^1O_2$ experiments than in the violanthrene experiments. However, this explanation is unsatisfactory, because ${}^1O_2$ quenching rate constants are insensitive to a fivefold increase in oxygen concentration (Table III). If reversible energy transfer were occurring, then an effect on k_q should be apparent with the inefficient quenchers in Table III.

The fact that an aromatic amino group in the *p*-phenylenediamine moiety is apparently necessary for high ${}^1O_2$ quenching efficiency (cf. Results) suggested a CT contribution to the ${}^1O_2$ quenching mechanism.[42] Azomethine dyes might be viewed simply as special cases of para-substituted anilines and, as such, they would be expected to quench ${}^1O_2$. Singlet-oxygen quenching rate constants for para-substituted *N,N*-dimethylanilines have been shown to correlate reasonably well with σ^- constants[9] ($\rho = -1.39$ in methanol). We therefore decided to measure the σ^- constant for a pyrazolone=N- moiety, in order to estimate the ${}^1O_2$ quenching efficiency for the appropriate azomethine dye assuming that the dye quenched by the same mechanism as the substituted anilines.



27

Compound **27** has a pK_a in 1:1 ethanol-water of 7.42. We established ρ for the ionization of para-substituted phenols in this solvent as 1.71, using readily available phenols and literature σ^- constants.[43] From the ρ value and the pK_a of phenol in this solvent (10.51), the calculated σ^- constant for this pyrazolone=N- substituent is 1.81.

The ${}^1O_2$ quenching efficiency ($k_q\tau$) of *N,N*-dimethylaniline was measured in pyridine solution and found to be $1.7 \times 10^3\ M^{-1}$. Assuming $\rho \simeq -1.4$ for pyridine,[44] then the calculated $k_q\tau$ value for dye **9**A is 5.2 M^{-1}. This is $10^{2.4}$ less than the measured value ($k_q\tau = 1.4 \times 10^3\ M^{-1}$), thus showing that the pyrazolone dye is a much better ${}^1O_2$ quencher than would be predicted on the basis of its being merely a substituted aromatic amine.

On the basis of the available data, we have concluded that neither an energy transfer nor a CT mechanism alone is sufficient to explain the present results. As a result, we propose a mechanism accommodating both of these features, namely, the formation of an excited complex between ${}^1O_2$ and azomethine dyes (eq 4). This type of mechanism

$$ {}^1O_2 + \text{dye} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^1(\text{excited complex}) \xrightarrow{k_2} {}^3O_2 + {}^3\text{dye} \qquad (4) $$

has been proposed by others to explain the quenching of ${}^1O_2$[9-11] and triplet ketones[45-47] by amines and the quenching of excited singlet states of electron-rich aromatic compounds by a number of organic compounds.[48,49]

For such a mechanism, the quenching rate constant is complex and will depend upon both the binding energy of the exciplex and the rate of the radiationless-decay step, k_2. Those factors that would increase the binding energy of the exciplex, such as charge transfer and low triplet energy of the quencher, should increase the observed quenching rate constant. In the case of amine quenching of ${}^1O_2$, the binding energy of the exciplex presumably arises from the contribution of the singlet CT state which, because it is energetically quite close to the triplet CT state,[50] requires a relatively small spin-orbit coupling to effect intersystem crossing[10] (eq 5). For azomethine dyes, energy transfer also may

$$ {}^1(\delta^- O_2 \ldots \delta^+ Q) \xrightarrow{\text{isc}} {}^3(\delta^- O_2 \ldots \delta^+ Q) \longrightarrow {}^3O_2 + Q \qquad (5) $$

contribute to the binding energy of the exciplex (eq 6). As a

$$ [{}^1({}^1O_2 \ldots Q) \longleftrightarrow {}^1({}^3O_2 \ldots {}^3Q)] \longrightarrow {}^3O_2 + {}^3Q \qquad (6) $$

result, the radiationless-decay step may be spin allowed.

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(26) Quenching rate constants were calculated using our β values for 2-methylpentene-2 in the appropriate solvent and the following lifetimes of $^1O_2$: benzene, 24 μsec;[15] pyridine, 33 ($\pm$15) μsec;[27] acetonitrile, 30 μsec.[15]
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(41) Plots of log k_{et} vs. E_T, such as that shown in Figure 3, reach plateaus at log $k_q \simeq 9.5$ when E_T = 40–48 kcal/mol for yellow dye quenchers only. The vertical triplet energy in the dyes is near that point where the efficiency of the energy-transfer process begins to drop from its maximum value. With cyan and most magenta dyes, the triplet energies of the dyes are too low to permit discrimination between rates of energy transfer from currently available triplet sensitizers (cf. Table II).
(42) We attempted to measure polarographic half-wave oxidation potentials of several azomethine dyes in pyridine in order to obtain evidence for or against a CT contribution to the quenching reaction. Dc polarography with a dropping mercury electrode gave oxidation waves for several dyes, but cyclic voltametry (10 V/sec) indicated that the measured half-wave potentials were not thermodynamic since return waves were not obtained. We are indebted to Dr. Eric Brown for assistance in the electrochemical experiments.
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Reactions Involving Electron Transfer. VI. A Stereochemical Test for Anion Radical Intermediates in Additions to Carbonyl Compounds[1]

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Abstract: The cis enones **4** and **8**, which undergo rapid electron exchange with the corresponding radical anions resulting in isomerization to the trans isomers **5** and **9**, have been used to test for the presence of radical anions during addition reactions of MeLi, Me_2Mg, and Me_2CuLi and during reduction reactions with $LiAlH_4$, $Cr(en)_2(OAc)_2$, and Li and *t*-BuOH in liquid NH_3. In reactions with MeLi, Me_2Mg, and $LiAlH_4$, both the alcohol products and the recovered excess cis enone used were recovered without appreciable stereochemical isomerization indicating that these reactions occur by direct nucleophilic addition (eq 1). In reactions with Me_2CuLi and $Cr(en)_2(OAc)_2$, the excess enone recovered was almost completely isomerized to the trans isomer and in reduction with Li and *t*-BuOH in liquid NH_3, the excess enone recovered was partially isomerized. These results are compatible with the presence of an anion radical during reaction either as an intermediate in a two-stage addition process (eq 2) or, possibly, as a by-product formed during reaction (eq 3).

The addition of a nucleophilic reagent, $N:^-$, to a carbonyl compound is usually represented (eq 1) as a single stage redistribution of the electron pair of the nucleophile, $N:^-$, to form a new N–C bond in the adduct **1**. However, a second two-stage reaction pathway (eq 2) is clearly possible in which the first stage is a transfer of a single electron from the electron-rich nucleophile, $N:^-$, to the electrophilic carbonyl group. This initial electron transfer is then followed by a second step in which the intermediate radicals or radical ions **2** and **3** recombine to form the adduct **1**.

Although a distinction between these two mechanistic possibilities may initially appear rather esoteric, upon further reflection several consequences of practical importance in synthesis become apparent. For example, in any reaction where there is a distinct preference in activation energies for the reaction to proceed by the two-stage mechanism (eq 2), one would expect a correlation between the success of the overall reaction and the ease with which the nucleophile, $N:^-$, can denote an electron (measured as the oxidation potential of $N:^-$) and the carbonyl compound can ac-