extracted by Hurst and Schuster.[20]

(iv) Water is very closely approximated by both methods whereas methanol is not well-fitted by either.

(v) Δ_{C-Cl} appears to be negligible in comparison to Δ_{CH_2}, etc. Similarly, the ether linkage C–O–C has been assigned zero strength. This works well for 1,4-dioxane, but the acyclic ethers fall away from a good fit. Since calculated k_Δ values for diethyl ether and *tert*-butyl methyl ether are different from the experimental values by widely different amounts, it is thought unlikely that misassignment of Δ_{C-O-C} is the cause.

Conclusion

To a fair degree of approximation the solvent dependence of k_Δ is apparently capable of being broken down into component parts that may be identified with specific atomic groupings within the solvent molecule. This additive nature of k_Δ supports the contention that nonradiative decay results from collisional interactions between $O_2(^1\Delta_g)$ molecules and solvent molecules. The present work, taken together with recent $O_2(^1\Delta_g)$ lifetimes,[14–17,20] indicates that a simple relationship[11] between k_d and the solvent absorbances at 7880 and 1590 nm^{-1} is not tenable. Hurst and Schuster,[20] while retaining the basic concept of intermolecular electronic-to-vibrational energy transfer, prefer a mechanism based on exchange energy transfer rather than the dipole–dipole mechanism proposed earlier.[11] They invoke a relationship between the frequency of the solvent fundamental vibrational mode and the additivity factor. This removes attention from the overtone

and combination bands. Hurst and Schuster maintain[20] that the higher the solvent vibrational frequency, the further down the $O_2(^3\Sigma_g^-)$ vibrational ladder will a single quantum transfer take the system, thereby making available the larger Franck–Condon factors between the lower oxygen vibrations. This zeroth order approximation is fine-tuned by incorporating an "off-resonance factor" that is related to the energy difference between the vibronic transition of O_2 and the solvent vibrational level. The data presented here are supportive of this concept. They do indicate, however, that different arrangements of the carbon skeleton cause significant differences in the oxygen–solvent interactions. Concomitant differences in the vibrational frequencies attributable to C–H modes are not evident in the infrared region around 2200 cm^{-1}. It may be that the reason for the progression $\Delta_{CH_2} > \Delta_{CH_3} > \Delta_{CH}$ is concerned with subtle changes in the individual off-resonance parameters.

Photoprocesses in Diphenylpolyenes. 2. Excited-State Interactions with Stable Free Radicals[1]

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Abstract: Singlet and triplet quenching by two stable free radicals, viz., di-*tert*-butylnitroxy (DTBN) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTMP), have been studied with three all-trans α,ω-diphenylpolyenes, Ph(*t*-C≡C)$_n$Ph, $n = 2$–4, as excited-state substrates in different solvents. Data are presented for fluorescence quenching rate constants (0.8–2.1 $\times 10^{10}$ M^{-1} s^{-1} in cyclohexane/methanol), the fraction of singlet quenching events that result in triplet generation (0.06–0.60), and rate constants for triplet quenching (0.18–4.8 $\times 10^8$ M^{-1} s^{-1} in solvents ranging from dimethyl sulfoxide to cyclohexane). As with aromatic hydrocarbons, the dependence of triplet quenching rate constants for polyenes on triplet energy (E_T) is found to be parabolic; that is, they first decrease systematically on going from *trans*-stilbene ($n = 1$) to *trans*-1,6-diphenyl-1,3,5-hexatriene ($n = 3$) and then increase on going from the latter to *trans*-1,8-diphenyl-1,3,5,7-octatetraene ($n = 4$). Possible interactions in terms of charge transfer, energy transfer, and electron exchange as well as roles of torsional motions and twisted configurations of polyenes in the quenching processes are discussed.

Molecular oxygen in its triplet ground state is by far the most commonly encountered paramagnetic species that has been studied extensively for its involvement in photoprocesses, particularly in enhancing spin-forbidden transitions through bimolecular or other types of interactions. Analogous paramagnetic effects[2] are expected from free radical doublets, although complications and

differences may arise from potential contributions of energy transfer and charge transfer. In fact, stable free radicals such as nitric oxide, di-*tert*-butylnitroxy (DTBN), and piperidinyl-1-oxy derivatives have been shown to be efficient quenchers of photoexcited species such as triplets,[3–7] singlets,[8–10] and excimers.[12]

(1) (a) The work described herein is supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2417 from the Notre Dame Radiation Laboratory. (b) Paper 1: Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 4507–4514. We regretfully note that ref 36 in paper 1 has been misquoted. A proper reference dealing with oxygen quenching of β-carotene triplet via spin-exchange mechanism should be: Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395–427.

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A wide variety of molecules of photophysical, photochemical, and biological interest have been examined for excited-state-mediated interactions with stable free radicals, some examples being aromatic hydrocarbons (ArH),[3,5b,6c,7-10,12] aromatic ketones,[7a,11] cyanine dyes,[5a,6a,b] stilbenes,[7] retinals,[4] and tris(2,2'-bipyridine)-ruthenium(II).[6c] In particular, DTBN has been often used as a probe (triplet quencher) in mechanistic studies of photochemical reactions.[7,11,13]

In a previous paper[1b] related with photoprocesses in diphenylpolyenes, we have dwelt on a number of singlet- and triplet-related photophysical behaviors of these polyene systems as revealed by low-resolution spectroscopy and nanosecond laser flash photolysis. We have noted that in many respects the excited-state dynamics of the polyenes, including the effects of oxygen and heavy-atom-containing quenchers, are very different from analogous phenomena observed for aromatic hydrocarbons; qualitatively, the differences have been attributed to torsional motions and/or twisted configurations (excited state) implicated in the case of polyenes. The present paper deals with the results of a similar study concerning the quenching of singlet and triplet excited states of the three α,ω-diphenylpolyenes (trans) by two stable free radicals, namely, DTBN and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTMP). Motivation in this work

DTBN   HTMP   Tempo
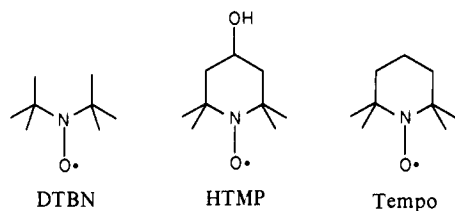
has come in part from the reported observations concerning high bimolecular rate constants (10^8–5×10^9 M^{-1} s^{-1}) for the quenching of stilbene triplets[7a] by DTBN and of retinal triplets[4] by HTMP.

The abbreviations used for the all-trans diphenylpolyenes under study are DPB for 1,4-diphenyl-1,3-butadiene, DPH for 1,6-diphenyl-1,3,5-hexatriene, and DPO for 1,8-diphenyl-1,3,5,7-octatetraene.

Experimental Section

The nitroxy radicals HTMP and DTBN were purchased from Aldrich and Eastman, respectively; the former was recrystallized twice from cyclohexane and the latter was used without further treatment. The sources and purification of diphenylpolyenes and some of the solvents are described in the previous paper[1b] of this series. Glycol (Fisher), tetrahydrofuran (Burdick and Jackson), N-methylformamide (Eastman), N,N-dimethylformamide (Fisher), and dimethyl sulfoxide (Aldrich) were distilled once before use. Acetone (Fisher), acetonitrile (Aldrich), and 2-propanol (Baker) were of spectrophotometric grade and were used without further treatment.
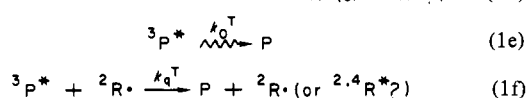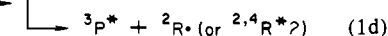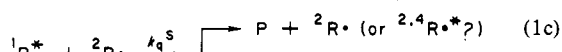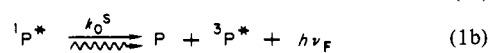
Details of equipment and experimental procedures used for fluorescence measurements and laser flash photolysis are given in the previous paper[1b] of this series. For some laser-photolysis experiments, the third harmonic (355 nm, ~6 ns, 2–5 mJ/pulses) from a Nd-YAG laser system (Quanta-Ray) was used for excitation.

Results

Neither of the two nitroxy radicals used as quenchers at concentrations <3 mM has any significant absorption at wavelengths longer than 520 nm. Moreover, windows are available at 335–345 nm for DTBN and at 330–390 nm for HTMP where the extinction

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coefficients of absorption by the radicals are very small (<3 M^{-1} cm^{-1}); these can be utilized for lamp and laser excitation for fluorescence-quenching measurements and for flash-photolytic observation of triplet-yield enhancement, respectively. Higher radical concentrations (up to 20 mM) were necessary to see sufficient quenching of triplet decay in some solvents; partial screening of laser photons by quenchers in these measurements posed no problem for measurement of triplet-decay rate constants because the triplet yield was enhanced at high radical concentrations; in fact, to avoid a second-order component in triplet decay, it was necessary to lower the laser intensity by defocusing the laser beam or by use of neutral density filters.

The experimental data in the present work consist of (i) Stern–Volmer constants (K_{SV}^F) for steady-state fluorescence quenching, (ii) quenching constants (K_{SV}^T) obtained from a Stern–Volmer type treatment of triplet-yield enhancement data from laser flash photolysis and fractions (δ) of singlet quenching events that result in triplet formation, and (iii) bimolecular rate constants (k_q^T) for triplet quenching. The over-all singlet- and triplet-mediated processes under consideration are shown in the following simplified scheme (P $\equiv$ polyene substrate; R$\cdot$ $\equiv$ radical quencher), based on competing intramolecular first-order and bimolecular quenching processes.

$$P \xrightarrow{h\nu} {}^1P^* \tag{1a}$$

$$^1P^* \xrightarrow{k_0^S} P + {}^3P^* + h\nu_F \tag{1b}$$

$$^1P^* + {}^2R\cdot \xrightarrow{k_q^S} \begin{cases} P + {}^2R\cdot \; (or \; {}^{2,4}R\cdot^* ?) \\ {}^3P^* + {}^2R\cdot \; (or \; {}^{2,4}R^* ?) \end{cases} \tag{1c, 1d}$$

$$^3P^* \xrightarrow{k_0^T} P \tag{1e}$$

$$^3P^* + {}^2R\cdot \xrightarrow{k_q^T} P + {}^2R\cdot \; (or \; {}^{2,4}R^* ?) \tag{1f}$$

Complications from involvement of twisted configurations and aspects of spin conservation in the interaction of a doublet with a triplet or a singlet will be considered later. On the basis of steps 1a–f, the following relationships can be easily derived.

$$\frac{I_0^F}{I^F} = 1 + K_{SV}^F[R\cdot] \tag{2}$$

$$K_{SV}^F = k_q^S / k_0^S \tag{3}$$

$$\left(\frac{\Delta OD^T}{\Delta OD_0^T} - 1\right)^{-1} = \left(\frac{\delta}{\phi_0^T} - 1\right)^{-1}\left[1 + \frac{1}{K_{SV}^T[R\cdot]}\right] \tag{4}$$

$$k_{obsd}^T = k_0^T + k_q^T[R\cdot] \tag{5}$$

In the above equations, I^F, ΔOD^T, and k^T_{obsd} are fluorescence intensity, transient absorbance (end-of-pulse) due to polyene triplet, and polyene triplet decay rate constant (first order), respectively, at radical concentration [R$\cdot$], and I_0^F, ΔOD_0^T, and k_0^T are the corresponding quantities in the absence of the quencher. $1/k_0^S$ and ϕ_0^T are fluorescence lifetime and triplet yield of the polyenes (in the absence of a quencher). Data concerning k_0^S, k_0^T, and ϕ_0^T under the conditions of our experiments are available in ref 1b.

Figure 1 shows two experimental traces for transient triplet absorption observed on laser excitation (337.1 nm) of *trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) in methanol in the presence of 7 mM DTBN and in its absence. This figure illustrates spectacular enhancement of triplet yield (by a factor of five in the given case) as well as shortening of triplet lifetime in the presence of the radical. Figure 2, parts A and B, and Figure 3A show some plots based on eq 2, 4, and 5, respectively. While the slopes of the linear plots in Figures 2A and 3A gave K_{SV}^F and k_q^T, respectively, δ/ϕ_0^T and K_{SV}^T were obtained from intercepts and intercept-to-slope ratios, respectively, of the plots shown in Figure 2B. Understandably, the errors in the determination of K_{SV}^T are much larger than the errors in K_{SV}^F; from measurement to measurement, the variations in the slope and the intercept of the double reciprocal

Table 1. Kinetic Data Concerning Singlet and Triplet Quenching of Diphenylpolyenes by Di-*tert*-butylnitroxy (DTBN) and 4-Hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTMP) Radicals

polyene	solvent	quencher	$K_{SV}^{F,a}$ 10^2 M^{-1}	$K_{SV}^{T,b}$ 10^2 M^{-1}	$k_q^{S,c}$ 10^{10} M^{-1} s^{-1}	$\delta/\phi_0^{T,d}$	δ^e	$k_q^{T,f}$ 10^7 M^{-1} s^{-1}
stilbene	cyclohexane							170
DPB	cyclohexane	DTBN	1.3	1.3	2.1	3.2	0.06 (0.06)	48
		HTMP	0.50	1.0	0.88	4.7	0.09 (0.15)	40
	methanol	DTBN						11
DPH	cyclohexane	DTBN	2.2	1.5	1.7	11	0.32 (0.25)	11
		HTMP	1.5	0.9	1.2	17	0.48 (0.32)	9.3
	methanol	DTBN	1.0	1.4	1.9	11	0.17 (0.24)	5.7
		HTMP	0.68	0.81	1.3	15	0.23 (0.25)	3.2
	benzene	DTBN	0.76	1.1	1.1	10	0.29 (0.37)	3.3
DPO	cyclohexane	DTBN	1.0	1.3	1.5	51	0.26 (0.30)	22
		HTMP	0.70	0.74	1.0	108	0.54 (0.80)	19
	methanol	DTBN	0.61	1.3	0.90	51	0.23 (0.49)	10
		HTMP	0.53	0.67	0.78	74	0.37 (0.44)	8.7

^{a} Stern–Volmer constants for steady-state fluorescence quenching (slopes of plots based on eq 2); ±15%. ^{b} Intercept-to-slope ratios from plots based on eq 4; ±50%. ^{c} Calculated from the relationship $K_{SV}^F = k_q^S \tau^F$ where τ^F is the observed fluorescence lifetime (taken from ref 1b). ^{d} Obtained from the intercepts of the plots based on eq 4; ±10%. ^{e} Calculated from δ/ϕ_0^T values in column 7, by using ϕ_0^T data from ref 1b. The values in the parentheses were obtained from δ/ϕ_0^T values determined from the slopes of plots based on eq 6. ^{f} Slopes of the plots based on eq 5; ±10%.
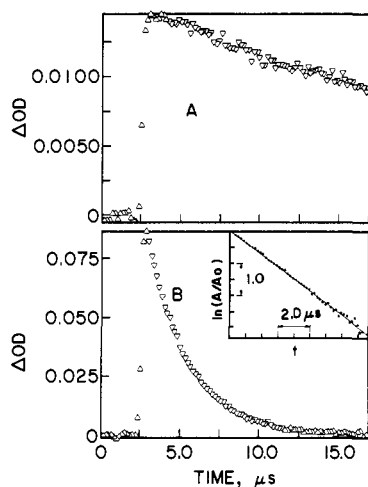

Figure 1. Experimental traces for transient absorption due to the DPH triplet at 410 nm in (A) deaerated methanol and (B) deaerated methanol containing 7.0 mM DTBN. The inset shows the fit of the portion of the kinetic profile B indicated by inverted triangles into the integrated equation for first-order decay.
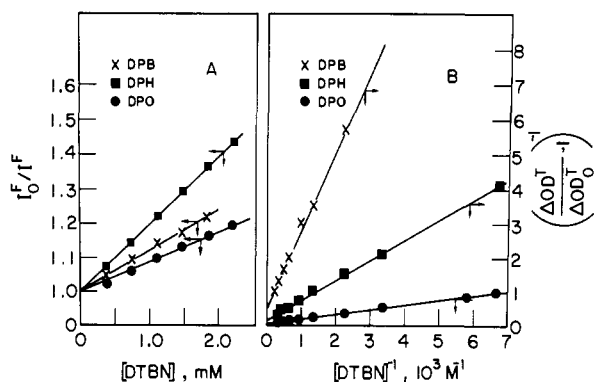

Figure 2. Representative plots based on (A) eq 2 (fluorescence quenching) and (B) eq 4 (triplet yield enhancement). Quencher, DTBN; solvent, cyclohexane.

plots based on eq 4 (Figure 2B) occur in opposite directions.

Table I summarizes the data concerning K_{SV}^F, K_{SV}^T, δ, and k_q^T with DTBN and HTMP as radical quenchers. Unless there is further interaction in the course of the formation of the observable triplet from the fluorescing singlet (i.e., in addition to the quenching of the fluorescing singlet), one would expect K_{SV}^F to
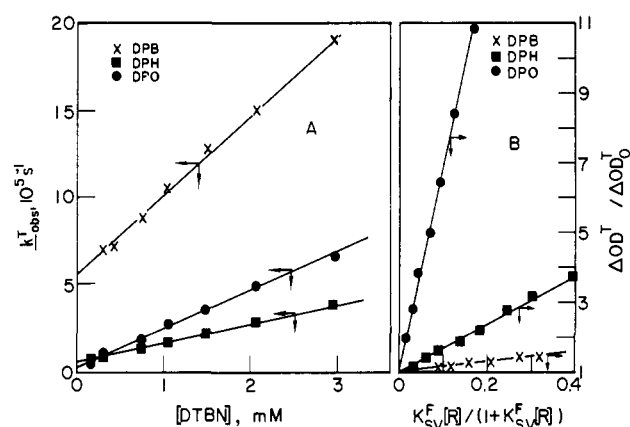

Figure 3. (A) Typical plots for triplet quenching by DTBN in cyclohexane. (B) Plots based on eq 6 using data for DTBN in cyclohexane.

be equal to K_{SV}^T. The overall impression one obtains after comparison of K_{SV}^F and K_{SV}^T data in Table I is that although there is discrepancy between K_{SV}^F and K_{SV}^T in many cases, this discrepancy is rather random, and appears to be primarily a reflection of the large errors associated with the measurement of K_{SV}^T. In principle, one can use the experimental parameter K_{SV}^F, which is more accurately determined, to replace K_{SV}^T in eq 4, which on rearrangement gives eq 6 for enhancement of triplet yield.

$$\frac{\Delta OD^T}{\Delta OD_0^T} = 1 + \left(\frac{\delta}{\phi_0^T} - 1\right)\frac{K_{SV}^F[R\cdot]}{1 + K_{SV}^F[R\cdot]} \qquad (6)$$

Equation 6 enables us to determine δ by plotting data concerning triplet-yield enhancement in terms of $\Delta OD^T/\Delta OD_0^T$ vs. $K_{SV}^F[R\cdot]/(1 + K_{SV}^F[R\cdot])$. Three such plots are shown in Figure 3B. δ values obtained in this manner are given in the parentheses of column 8 in Table I. Obviously, differences in δ values calculated by the two methods are pronounced in the cases where differences between K_{SV}^T and K_{SV}^F are also high.

In some works,[3,5a,6c] charge-transfer interaction has been implicated in the quenching of triplets by nitroxy radicals; with some cyanine dyes,[5a] the radical cation of the substrate has been shown to be a transient photoproduct by flash photolysis. We have measured the absorption spectra of transients formed as a result of the laser flash photolysis of the three polyenes in cyclohexane and methanol in the presence of the excess of radical quenchers. While the end-of-pulse absorption spectra were identical with those of the polyene triplets,[1b] there were practically no residual absorptions following the decay of the triplets. Since diphenylpolyene radical cations are known[14,15] for their intense absorptions at

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Table II. Rate Constants for Quenching of DPH and DPO Triplets by DTBN in Various Solvents

solvent	dielectric constant[a]	k_q^T,[b] 10^7 M^{-1} s^{-1}	
		DPH	DPO
acetone	20.7	2.0	4.5
tetrahydrofuran	7.58	2.2	5.0
acetonitrile	37.5	1.9	5.4
N-methylformamide	182.4	2.2	6.0
N,N-dimethylformamide	36.7	2.0	4.4
dimethylsulfoxide	46.7	1.8	5.1
2-propanol	19.9	3.4	7.0
glycol	37.7	3.4	6.2
benzene	2.3	3.3	6.7

[a] From ref 29a–c; all at 25 °C, except acetonitrile for which the quoted value is at 20 °C. [b] ±10%.

Table III. Activation Parameters for Triplet Quenching by DTBN in Methylcyclohexane

triplet	k_q^T(22 °C), M^{-1} s^{-1}	E_a, kcal/mol	$\log A^a$
DPH	8.6×10^7	1.0	8.7
DPO	1.8×10^8	0.33	8.5
anthracene	7.8×10^6	1.2	7.8

[a] A is in M^{-1} s^{-1}.

500–700 nm, we can conclude that singlet- and triplet-mediated, charge-transfer interactions, operative or not, do not lead to separation into radical ions in cyclohexane or methanol.

The possible involvement of charge transfer in the quenching of DPH and DPO triplets by DTBN has also been examined from the point of view of the effect of solvent polarity of k_q^T. The data are given in Table II. Relative to cyclohexane (Table I) k_q^T's are smaller in benzene as well as in all of the polar/H-bonding solvents (Table II). The fact that k_q^T for DPO is 2–3 times higher than that for DPH is maintained in all of the solvents examined.
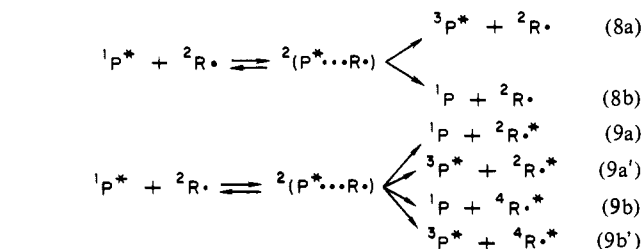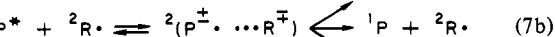
We have also examined the temperature dependence of k_q^T for DPO, DPH, and anthracene (for comparison) using DTBN as the quencher in methylcyclohexane. At or below 203 K, DTBN-enhanced formation of DPO and DPH triplets at [DTBN] ≤ 0.1 M is very small (possibly because of low k_q^S); therefore, no measurement concerning triplet quenching for these systems was feasible at or below 203 K. The Arrhenius plots for k_q^T are reasonably linear over the temperature range used (203–333 K). The activation parameters are given in Table III.

Discussion

It is worthwhile to begin by pointing out the salient features in our results concerning the quenching of excited states of diphenylpolyenes by nitroxy radicals as well as noting the points of similarity and difference with respect to the results of analogous studies with aromatic hydrocarbons (ArH) and other systems (e.g., carbocyanine dyes). First, the rate constants (k_q^S) for the quenching of fluorescence are all in the limit of diffusion control and show practically no dependence on polyene chain length or on solvent nature (cyclohexane vs. methanol). k_q^S data for polyenes with DTBN and HTMP as quenchers are comparable in magnitudes with those reported for ArH fluorescence quenching by DTBN[8] and 2,2,6,6-tetramethylpiperidinyl-1-oxy[9a] (Tempo) radical. A close comparison of k_q^S data for DTBN and HTMP shows that the former is a slightly better quencher for polyene singlets in both cyclohexane and methanol (Table I). Second, the fraction (δ) of the polyene singlet quenching events that produce triplets is small in the case of DPB (6–15%); δ increases on increasing the chain length (0.25–0.65 for DPH and DPO), but remains much smaller than the efficiency of unity. In other words, the singlet-mediated interaction results in an enhanced overall $S_1 \rightsquigarrow S_0$ process to an extent comparable to, or more

than, that of the enhanced $S_1 \rightsquigarrow T_1$ process. Analogous estimates[10] for 9,10-dimethylanthracene, 9,10-diphenylanthracene, and perylene gave 0.94, 0.74, and 0.84 for δ for singlet quenching by HTMP, suggesting the dominance of enhanced intersystem crossing in the case of ArH's. Third, under comparable conditions, the polyene triplets are quenched by nitroxy radicals with significantly higher rate constants (k_q^T) than those for ArH triplets. For example, DPH triplet ($E_T \sim 34$ kcal/mol) with the lowest k_q^T among the diphenylpolyenes (Table I) is quenched by DTBN with a rate constant of 1.10×10^8 M^{-1} s^{-1} (in cyclohexane); this value is higher than k_q^T (1.1×10^7 M^{-1} s^{-1} in cyclohexane) for perylene ($E_T = 35.1$ kcal/mol) by an order of magnitude. On the other hand, for *all-trans*-retinal, a polyene with six double bonds and E_T (~ 36 kcal/mol)[16] close to that of DPH, the triplet quenching by HTMP occurs with rate constants ($1–10 \times 10^8$ M^{-1} s^{-1})[4] that are higher than those observed for DPH triplets under similar conditions. Higher k_q^T's are also noted for carbocyanine dye triplets[5a] for which charge-transfer interactions have been shown to be operative. More concerning the factors responsible for higher k_q^T's in the case of polyenes relative to ArH's will be considered later. Fourth, as observed with ArH's[3,5b,9b] and retinals,[4] there is no well-defined correlation between k_q^T's and solvent polarity (Table II). In general, k_q^T's for both DPH and DPO decrease rather sharply on going from a nonpolar solvent (cyclohexane) to a moderately polar one (e.g., tetrahydrofuran) and change very little upon varying dielectric constant among the polar/H-bonding solvents (Tables I and II). It should be noted that the lowering of k_q^T in polar/H-bonding solvents and in benzene can arise because of solvation[5b,17] of the free radical, i.e., engagement of the unpaired electron in dipole–dipole interaction, hydrogen bonding, and interaction with aromatic π clouds. Fifth, δ values do not show any significant dependence on solvent nature (cyclohexane, methanol, and benzene). Also, the nature of the free radical, DTBN vs. HTMP, does not have any effect on δ values. Sixth, the activation energies for triplet quenching are low, and are similar to those obtained[18] for ArH's by using Tempo as the quencher in 2,2,4-trimethylpentane. It appears that, relative to ArH triplets, the larger k_q^T's for polyene triplets arise to a large extent from less stringent entropic requirements. The increase in k_q^T on going from DPH to DPO is, however, primarily a result of pronounced decrease in activation energy (Table III).

A. Singlet Quenching. A variety of mechanisms are possible for the quenching of a singlet excited state by a free radical (doublet). These include charge transfer, spin exchange, and energy transfer and are represented in eq 7, 8, and 9, respectively.

$$^1P^* + {}^2R\cdot \rightleftharpoons {}^2(P^{\pm}\cdots R^{\mp}) \begin{cases} {}^2P^{\cdot\pm} + R^{\mp} & (7a) \\ {}^1P + {}^2R\cdot & (7b) \\ {}^3P^* + {}^2R\cdot & (7c) \end{cases}$$

$$^1P^* + {}^2R\cdot \rightleftharpoons {}^2(P^*\cdots R\cdot) \begin{cases} {}^3P^* + {}^2R\cdot & (8a) \\ {}^1P + {}^2R\cdot & (8b) \end{cases}$$

$$^1P^* + {}^2R\cdot \rightleftharpoons {}^2(P^*\cdots R\cdot) \begin{cases} {}^1P + {}^2R\cdot^* & (9a) \\ {}^3P^* + {}^2R\cdot^* & (9a') \\ {}^1P + {}^4R\cdot^* & (9b) \\ {}^3P^* + {}^4R\cdot^* & (9b') \end{cases}$$

Process 9b representing enhanced internal conversion via energy transfer to form a quadruplet state of the free radical is not allowed under spin conservation and hence may be disregarded. The nitroxy radicals are characterized by a weak and broad absorption band system at 400–590 nm that has been assigned[8] to a symmetry-forbidden spin-allowed (doublet–doublet) transition of n,π*

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Table IV. Comparison of Enhancement of Intersystem Crossing of Diphenylpolyenes by O_2, Ethyl Iodide, and Nitroxy Radicals in Cyclohexane

poly-ene	k_{isc},[a] s^{-1}	$k_q{}^S\delta$, s^{-1}			
		O_2[a]	EtI[a]	DTBN[b]	HTMP[b]
DPB	3.3×10^7		1.7×10^9	1.3×10^9	1.3×10^9
DPH	2.2×10^6	1.4×10^{10}	1.0×10^8	4.3×10^9	3.8×10^9
DPO	7.5×10^5	1.5×10^{10}	6.0×10^6	4.5×10^9	6.4×10^9

[a] Data taken from ref 1b.   [b] $k_q{}^S$ given in column 6 of Table I and δ given in the parentheses in column 8 of Table I have been used to calculate $k_q{}^S\delta$.

character. Since the polyenes under consideration have singlet energies (E_S = 62–80 kcal/mol) higher than the energy of this transition, singlet energy transfer between $^1P^*$ and $^2R\cdot$ (eq 9a) would be exothermic. However, a detailed consideration by Green et al.[8] based on the results of fluorescence quenching of ten ArH's (E_S = 50–92 kcal/mol) by DTBN has ruled out singlet energy transfer by resonance or collisional interactions.[19,20] The same authors[8] also argued against the charge-transfer mechanism (eq 7a–c) on the basis of a lack of solvent dependence of $k_q{}^S$. We also do not see any significant difference in $k_q{}^S$ for DPH and DPO on going from cyclohexane to methanol; we are, however, reluctant to take this as evidence against the charge-transfer mechanism because the singlet quenching for all of the three polyenes occurs in the limit of diffusion control and may not be differentiated by solvent polarity. Furthermore, the straightforward reasoning is hampered by the complication in the solvent effect arising from the susceptibility of the radical site to solvation. However, the complete lack of formation of polyene radical ions in polar solvents as a result of singlet quenching argues strongly against a mechanism involving extensive charge transfer between the partners in the course of the quenching process.

It is highly unlikely that a charge-transfer mechanism alone would be totally responsible for the formation of polyene triplets as a result of singlet quenching (particularly in the case of DPH and DPO where δ's are relatively high). Spin-exchange interactions represented by eq 8a and 8b leading to enhanced intersystem crossing and enhanced internal conversion, respectively, are both spin allowed, and are expected to contribute to the singlet quenching. We, however, cannot sort out the relative importance of charge-transfer and spin-exchange interaction in the overall singlet quenching or in the enhanced intersystem crossing (that is, processes 7c and 8a).

It is of interest to examine how polyene singlet quenching by nitroxy radicals compares with that by oxygen[1b] and ethyl iodide.[1b] In Table IV, data regarding enhanced intersystem crossing measured in terms of $k_q{}^S\delta$ have been compiled for the three types of quenchers. The three diphenylpolyenes form a closely related class where the rate constant (k_{isc}) for intersystem crossing is found to decrease systematically as the polyene chain length is increased (column 2 of Table IV). In terms of Franck–Condon factors[21a,b] as applied to spin-exchange[3,7a] and heavy-atom[22] interactions, one would expect a parallelism between k_{isc} and $k_q{}^S\delta$. The data in Table IV indicate that this parallelism is followed only in the case of the quenching by ethyl iodide. For O_2 as the quencher, $k_q{}^S\delta$ values are very high, and remain unchanged between DPH and DPO as fluorophores. On the other hand, for the nitroxy radicals, $k_q{}^S\delta$ values show an increasing trend on increasing polyene chain length, particularly on going from DPB to DPH. Thus, $k_q{}^S\delta$ does not correlate with k_{isc} in the case of nitroxy radicals.

Another interesting observation concerns the variation of δ as a function of the nature of the quenchers. Among O_2, ethyl iodide, and nitroxy radicals, we note that δ values for DPH and DPO vary in the order O_2 > DTBN ~ HTMP > EtI. One possible
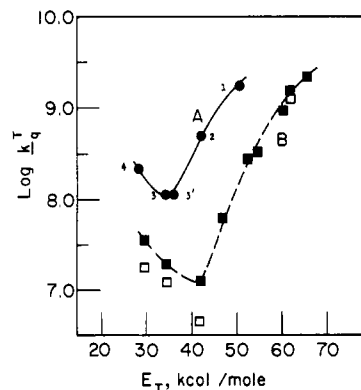

Figure 4. Logarithmic plots of triplet quenching rate constants (by DTBN) vs. triplet energies. Plot A corresponds to diphenylpolyenes with $k_q{}^T$ data (in cyclohexane) from the present work and E_T data taken from ref 28a–c. E_T data of diphenylpolyenes were obtained from $T_1 \leftarrow S_0$ absorption of stilbene (1), DPB (2), and DPH (3) and from energy-transfer kinetics in the case of DPH (3') and DPO (4). Plot B is based on $k_q{}^T$ (in hexane) and E_T data of aromatic hydrocarbons taken from ref 3; the open squares represent $k_q{}^T$ data for phenanthrene, anthracene, perylene, and naphthacene in cyclohexane (obtained in the present study).

reason for this can be that the relative contribution of charge-transfer interactions leading to enhanced internal conversion follows this order. Also, between O_2 and a nitroxy radical, it seems plausible that while O_2 is capable of catalyzing intersystem crossing (eq 10) of diphenylpolyenes ($\Delta E_{S_1-T_1}$ = 28–36 kcal/mol) by

$$^3O_2 + {}^1P^* \rightarrow {}^3P^* + {}^1O_2 \qquad (10)$$
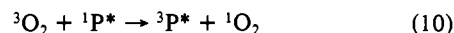
exothermic energy transfer, such an efficient channel (eq 9a') of intersystem crossing via energy transfer[23] is not feasible for a nitroxy radical ($^2R_1\cdot-^2R\cdot^*$ gap being ~48 kcal/mol).

B. Triplet Quenching. Perhaps the most interesting findings in the present study lie in the data concerning polyene triplet quenching by nitroxy radicals. In Figure 4 we have shown plots of log $k_q{}^T$ vs. E_T using $k_q{}^T$ data for diphenylpolyenes (in cyclohexane) and ArH's (in hexane, taken from ref 3) with DTBN as the quencher in both cases. The E_T data for diphenylpolyenes are those obtained from $T_1 \leftarrow S_0$ absorption or energy-transfer kinetics and do not represent vertical energy gaps at distorted triplet geometries that are probably involved in the quenching interaction (see later). The parabolic curve (Figure 4A) for diphenylpolyenes is located much above the similar curve for ArH's (Figure 4B). It is also displaced to the left; that is, the minimum occurs at a lower triplet energy (34 kcal/mol, corresponding to DPH) than that for ArH's (E_T for the minimum is 42 kcal/mol, corresponding to anthracene). A few data points for $k_q{}^T$ for ArH triplets using DTBN in cyclohexane, obtained in the present work, are also shown in Figure 4; this is to stress the fact that in the same solvent, cyclohexane, the difference between $k_q{}^T$'s for a diphenylpolyene and an ArH of comparable triplet energy is even more pronounced.

As in the case of singlet stilbene,[24] (vide supra), three principal mechanisms, namely, charge transfer,[3,5a] energy transfer,[5b,9b] and spin exchange,[3,5a,b,7a,9b] have been invoked from time to time to explain triplet quenching by nitroxy radicals. There is a general consensus that spin-exchange interaction[2] represented by eq 12a, dominates in the falling portion of curve B in Figure 4 at low triplet energies ($E_T \le 42$ kcal/mol). For the rising part, Gijzeman et al.[3] offered an explanation by implicating charge-transfer states in the collision complex formed from the excited state and the nitroxy quencher. Watkins,[9b] however, failed to observe a cor-

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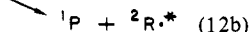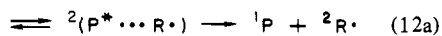
relation between k_q^T (by Tempo) and charge-transfer properties of ArH–nitroxy collision complexes and, hence, ruled out charge transfer as a viable mechanism. Watkins[9b] as well as Kuzmin et al.[5b] proposed energy transfer (eq 12b) as the mechanism that

$$^3P^* + {}^2R\cdot \rightleftharpoons {}^4(P^*\cdots R\cdot) \longrightarrow {}^1P + {}^4R\cdot^* \quad (11)$$

$$\rightleftharpoons {}^2(P^*\cdots R\cdot) \longrightarrow {}^1P + {}^2R\cdot \quad (12a)$$

$$\searrow {}^1P + {}^2R\cdot^* \quad (12b)$$

dominates at relatively high triplet energies. Diphenylpolyenes appear to offer no new facet relative to ArH's as far as the relative importances of energy transfer and charge transfer in the triplet quenching process are concerned. On the other hand, in the spin-exchange mechanism the polyene excited states may play dramatically different roles through involvement of torsional motions and/or perpendicular geometries. Two approaches deserve consideration.

First, as is the case with stilbene,[24] the polyene triplets exist in a fluid solution as an equilibrium mixture of planar (transoid, $^3P^*_t$) and twisted (perpendicular, $^3P^*_p$) forms (see eq 13). With

$$^3P^*_t \overset{K}{\rightleftharpoons} {}^3P^*_p \quad (13)$$

the assumption that the equilibrium is maintained fast during the quenching process, k_q^T can be shown to be given by eq 14, where

$$k_q^T = (k_{q,t}^T + k_{q,p}^T K)/(1 + K) \quad (14)$$

$k_{q,t}^T$ and $k_{q,p}^T$ are the rate constants for bimolecular quenching of planar and perpendicular forms, respectively. From the golden rule[21a,b] of radiationless transitions, one would expect the rate constant ($k_{q,p}^T$) for the quenching of the perpendicular form ($^3P^*_p$) by a nitroxy radical to be large because the transition via spin exchange involves two states at twisted configurations that are close in energy and is associated with large Franck–Condon factors. Thus, although $k_{q,t}^T$ is small and comparable to that for an ArH triplet of similar E_T, the observed k_q^T may be large because of substantial contribution from $k_{q,p}^T$ (eq 14).

In the light of the model based on equilibrium between planar and perpendicular forms (eq 13) and the approximation $k_{q,t}^T \ll k_{q,p}^T$, the observed triplet quenching rate constant (k_q^T) is determined by K and $k_{q,p}^T$. Another important consideration in this context is that the possibility of equilibria involving multiple twisted forms exist for polyenes with two or more double bonds. The observed systematic decrease in k_q^T on going from stilbene to DPB to DPH (Figure 4A) is a reflection of a decrease in K's (that is, twisted forms of triplet becoming less important in longer chain polyenes) and/or a decrease in $k_{q,p}^T$'s (that is, larger vertical T_1–S_0 energy gaps and smaller Franck–Condon factors at twister geometries). The departure of DPO from this trend is explainable by the facts that the effect of the multiplicity of twisted forms becomes dominant in the case of this polyene and/or that a polarizability mechanism, as suggested[1b] for heavy-atom quenching, is operative.

The second approach, a general one for intrinsic or enhanced radiationless processes in polyenes, is based on the strong-coupling theory of Englman and Jortner[25a] (E–J). Just as in the case of the Landau–Zener theory[25b] that we used to discuss this problem in paper I, we cannot use this theory to its fullest advantage because we lack a knowledge of the details of T_1 and S_0 potential energy surfaces. Furthermore, if such a knowledge existed, we should use the treatment of Gelbart, Freed, and Rice[26] who treated the torsional motions as hindered rotations.

In spite of all these limitations, the E–J theory illustrates in a very elegant fashion how the energy gap law may be breaking down in polyenes. Using the generating function method of

Figure 5. Displaced harmonic potentials in E–J model. Dashed curves represent a schematic of T_1 and S_0 potential energy curves for the torsional motions in diphenylpolyenes.

Kubo,[27] Englman and Jortner derived the usual energy gap law as a weak-coupling limit to their general theory, and they also derived a result for a radiationless rate constant in the strong-coupling limit of their theory. The main result of the strong-coupling limit of the theory was

$$W = ([2\pi]^{1/2}C^2/D\hbar^2) \exp[-(\Delta E - E_M)^2/2D^2\hbar^2] \quad (15)$$

Here ΔE is the energy gap and E_M is the Stokes shift. For the displaced harmonic oscillators of the E–J theory, these two parameters are illustrated in Figure 5. In eq 15, C^2 is the square of the electronic matrix element between the two states, and D^2 is given by eq 16. In eq 16, ω_j is the frequency of the jth harmonic

$$D^2 \equiv (1/2)\sum_j \omega_j^2\Delta_j^2(2\bar{n}_j + 1) \simeq E_M\langle\omega\rangle \coth (\beta\hbar\langle\omega\rangle/2)/\hbar \quad (16)$$

oscillator, Δ_j is its displacement, $\bar{n}_j$ is its equilibrium population, and β is $1/kT$. $\langle\omega\rangle$ is the average frequency of the oscillators. In terms of these quantities

$$E_M = (1/2)\sum_j \hbar\omega_j\Delta_j \quad (17)$$

and the strong-coupling limit is valid for the condition that

$$(1/2)\sum_j |\Delta_j|^2(2\bar{n}_j + 1) \gg 1 \quad (18)$$

Physically eq 18 corresponds to the case where there are large displacements, Δ_j's, between the equilibrium nuclear configurations of the two electronic states.

The main point we want to make in displaying the E–J theory is that within a unified theory, it is possible to derive the energy gap law in one limit of the theory and to have it break down in the strong-coupling limit of the theory. In fact, as can be seen from eq 15 the rate constant, W, will not necessarily even decrease in a uniform fashion as the energy gap, ΔE, increases. Whether W increases or decreases with changes in ΔE depends on how E_M and D^2 change from molecule to molecule.

Finally we would like to suggest that it is precisely the strong-coupling limit that should be used in applying radiationless transition theories to the torsional motions in polyenes. If perpendicular, or nonplanar, triplets are likely, then the displacements, Δ_j, will be large and the strong-coupling condition in eq 18 will hold. A schematic representation of likely T_1 and S_0 curves for polyenes, which are superimposed on the E–J potential energy curves, is given in Figure 5.

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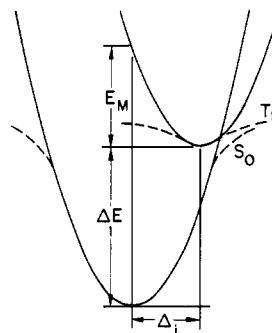(26) Gelbart, W. M.; Freed, K. F.; Rice, S. A. *J. Chem. Phys.* **1970**, *52*, 2460–2473.

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