

ROLE OF GEOMETRIC DISTORTION IN THE QUENCHING BEHAVIORS OF ALL-*trans* 1,4-DIPHENYL-1,3-BUTADIENE TRIPLET

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Summary

The quenching behaviors of all-*trans* 1,4-diphenyl-1,3-butadiene triplet towards azulene, ferrocene, perylene, oxygen and di-*tert*-butyl-nitroxide were examined in the context of those of several aromatic triplets with comparable spectroscopic triplet energies. The results are explained in terms of distortion of the diene triplet from its planar geometry.

1. Introduction

Evidence from steady state photochemical studies [1, 2] as well as relatively recent transient absorption spectral measurements [3 - 6] based on laser flash photolysis and pulse radiolysis strongly suggests that the triplets of stilbenes and related olefins exist in two forms, namely planar (transoid, $^3t^*$) and perpendicular ($^3p^*$) configurations, the latter arising from twisting around the olefinic double bond to 90° . The relative stabilization of the orthogonal form in the excited state is predicted by the theoretical calculations of Merer and Mulliken [7] and Orlandi and Siebrand [8]. Recent studies by Caldwell and Cao [9] of styrene derivatives have shown that the triplets of these olefins exist exclusively in the perpendicular form. In contrast, for stilbene [5] and 1-phenyl-2-(2-naphthyl) ethylene [6] the equilibrium constants for the $^3t^* \rightleftharpoons ^3p^*$ equilibria in benzene are estimated to be 8.0 and 1 - 2 respectively. The involvement of twisted geometries in the triplet excited states of olefins manifests itself in the following. First, the triplet lifetimes are relatively short presumably because of fast intersystem crossing in distorted geometries where the potential energy surfaces of the triplet and the ground state are close to one another. Second, differences are observed in the quenching behaviors toward specific quenchers such as azulene, ferrocene, oxygen and stable free radicals relative to the behaviors of a relatively rigid aromatic triplet with comparable triplet energy E_T because of relatively effective or ineffective roles of the twisted form in the quenching process.

It is of interest to see how the relative importance of planar and twisted forms changes as a function of polyene chain length on going from stilbene

to longer homologues. In particular, the diene all-*trans* 1,4-diphenyl-1,3-butadiene (DPB) is important because it represents the transition in the series from stilbene to long-chain polyenes. Geometric distortion in the excited state has featured strongly in the studies [10 - 12] concerning singlet-related photophysical behaviors of DPB. Although many of the triplet-related photophysical properties of DPB are now well-characterized [13 - 16], the specific question of the role of geometric distortion in the lowest triplet state has not been examined in detail, except for the fact that Görner [16] recently suggested that twisted geometries are relatively unimportant as far as the triplets of long-chain diphenylpolyenes are concerned.

In this work we have compared the quenching behaviors of DPB triplet (observed under direct excitation using nanosecond laser flash photolysis) with those of several aromatic triplets with triplet energies E_T close to that of DPB. The quenchers are azulene, ferrocene, perylene, oxygen and di-*tert*-butylnitroxide (DTBN). The results strongly suggest that in benzene there is a significant contribution from a twisted form of DPB triplet to the observed intersystem crossing ($T_1 \rightsquigarrow S_0$) and bimolecular quenching processes.

2. Experimental details

The following compounds, purchased from Aldrich, were recrystallized from the solvents given in parentheses: DPB (ethanol), anthracene (ANT) (benzene), 9,10-diphenylanthracene (DPA) (benzene) and 1-chloroanthracene (*n*-hexane). 3,4-benzopyrene (more than 99% pure), perylene (more than 99% pure), azulene (99% pure) and ferrocene, all Aldrich products, were used without further purification. DTBN from Eastman was used as received and ethyl iodide (EtI) from Aldrich was distilled under vacuum. The main solvent employed in this work was benzene (Aldrich, gold label); for some experiments, ethylene glycol (Fisher, distilled once under reduced pressure) and methanol (Aldrich, gold label) were also used. Varying concentrations of oxygen in solutions were obtained by bubbling with custom-made mixtures of oxygen and nitrogen (Linde Air Products). Deaeration was carried out by purging solutions with oxygen-free argon.

The laser flash photolysis set-up including the kinetic spectrophotometer used for measuring transient absorption is described elsewhere [15, 17]. Laser pulses (337.1 nm; about 8 ns; 2 - 3 mJ per pulse) from a UV-400 Moletron system were used for excitation. All bimolecular quenching rate constants were reproducible to within $\pm 10\%$.

3. Results

Direct laser excitation of DPB (0.1 - 0.5 mM) in benzene or ethylene glycol leads to very weak transient absorption signals due to its triplet. However, the triplet formation is significantly enhanced via heavy-atom-

induced intersystem crossing in the presence of EtI (0.1 - 0.6 M). While the triplet-triplet (T-T) absorption spectrum in benzene (Fig. 1, curve A) is broad and structureless with an absorption maximum at 405 nm, that in ethylene glycol (Fig. 1, curve B) displays poorly resolved vibronic bands at 393, 375 and 365 nm. The triplet decay, monitored at attenuated laser intensities, follows clean first-order kinetics; extrapolation of the triplet lifetimes measured with $[\text{DPB}] = 10^{-4} \text{ M}$ in benzene with various concentrations of EtI (0.1 - 0.6 M) gives a lifetime of $2.6 \pm 0.2 \mu\text{s}$ for the triplet and a bimolecular rate constant of $4.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for quenching by EtI. Also, measurements of the triplet lifetimes at $[\text{EtI}] = 0.06 \text{ M}$ as a function of DPB concentration in the range $10^{-4} - 10^{-3} \text{ M}$ give $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant for self-quenching (in benzene). As expected, the triplet lifetime observed in ethylene glycol is much longer ($5.0 \mu\text{s}$ at $[\text{DPB}] = 5 \times 10^{-4} \text{ M}$ and $[\text{EtI}] = 0.06 \text{ M}$).

Laser flash photolysis of a benzene solution containing ANT ($5 \times 10^{-4} \text{ M}$) and DPB ($5 \times 10^{-4} \text{ M}$) shows that the triplets of both substrates coexist during the decay of the transient absorption (following the initial fast formation process at or near the T-T maximum (405 nm) of DPB and concomitant decay at or near the T-T maximum (428 nm) of ANT). Similar observations in cyclohexane have been reported previously [15]. This suggests the reversibility [18] of the triplet energy transfer between DPB and ANT understandably because of the proximity of their triplet energies (see later):



In order to estimate the rate constant for energy transfer from ${}^3\text{ANT}^*$ to DPB, *i.e.* k_1 in eqn. (1), the decay rate constants of ${}^3\text{ANT}^*$ (monitored using

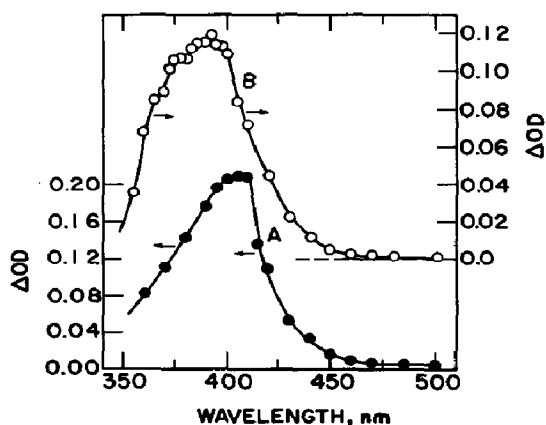


Fig. 1. T-T absorption spectra of DPB in benzene + 0.6 M EtI (curve A) and ethylene glycol + 0.3 M EtI (curve B) monitored at 300 ns and 500 ns respectively after the laser flash.

its T-T absorption at 428 nm) were measured as a function of the DPB concentration (0.2 mM or less) in the presence of 0.061 M DTBN. The purpose of adding DTBN was to render the lifetime of $^3\text{DPB}^*$ considerably short (105 ns) as a result of fast quenching by the free radical (see later) so that $k_d' + k_q^T[\text{DTBN}] \gg k_{-1}[\text{ANT}]$, k_q^T being the rate constant for DTBN quenching of $^3\text{DPB}^*$. The value of k_1 obtained in this manner is $(3.2 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This is comparable with a value determined recently for the ANT-DPA system [19].

Pseudo-first-order decay rate constants k_{obs}^T for triplets of DPB and several aromatic systems with E_T values of 40.9 - 42.5 kcal mol $^{-1}$ have been determined in benzene in the presence of various concentrations of azulene, ferrocene, perylene, oxygen and DTBN. The triplets were monitored at the respective absorption maxima, namely 405 nm, 428 nm, 445 nm, 475 nm and 435 nm for DPB, ANT, DPA, 3,4-benzopyrene and 1-chloroanthracene respectively. Since the intrinsic triplet yields of DPB and DPA are small [15, 19] the quenching experiments with their triplets were carried out in the presence of constant concentrations of EtI (0.6 M) for DPB and constant concentrations of DTBN (0.12 M) for DPA. EtI was found to be inefficient in effecting intersystem crossing in DPA. The bimolecular rate constants k_q^T for quenching were obtained from the linear plots based on the following equation:

$$k_{\text{obs}}^T = \tau_T^{-1} + k_q^T[Q] \quad (2)$$

where $[Q]$ is the quencher concentration at which k_{obs}^T is measured and τ_T designates the triplet lifetime in the absence of a quencher. Figure 2 shows some representative plots for the determination of k_q^T for ANT and DPB triplets. Data concerning k_q^T for benzene are presented in Table 1. It should

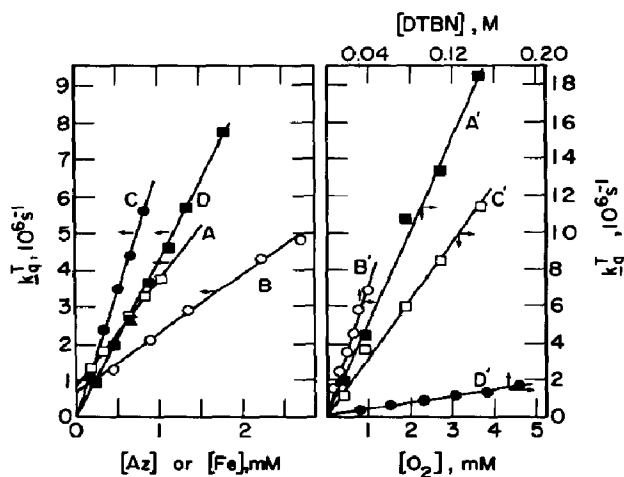


Fig. 2. Plots for quenching of DPB triplet and ANT triplet with various quenchers in benzene based on eqn. (2): curve A, $^3\text{DPB} + \text{azulene}$; curve B, $^3\text{DPB} + \text{ferrocene}$; curve C, $^3\text{ANT} + \text{azulene}$; curve D, $^3\text{ANT} + \text{ferrocene}$; curve A', $^3\text{DPB} + \text{oxygen}$; curve B', $^3\text{DPB} + \text{DTBN}$; curve C', $^3\text{ANT} + \text{oxygen}$; curve D', $^3\text{ANT} + \text{DTBN}$.

TABLE 1

Rate constants for triplet quenching in benzene at 298 K.

Triplet	E_T^a (kcal mol ⁻¹)	k_q^T ^b (M ⁻¹ s ⁻¹) for the following quenchers				
		Azulene	Ferrocene	Perylene	Oxygen	DTBN
ANT	42.5	6.7×10^9	4.2×10^9	5.1×10^9	3.1×10^9	8.8×10^6
1-chloro- anthracene	42.1	5.9×10^9	4.7×10^9		2.8×10^9	7.1×10^6
3,4-benzo- pyrene	41.9	5.6×10^9	4.5×10^9	4.8×10^9	3.2×10^9	8.0×10^6
DPA	40.9	2.5×10^9	1.6×10^9		1.9×10^9	5.1×10^6
DPB	42.3	2.9×10^9	1.6×10^9	3.0×10^9	5.0×10^9	1.5×10^8

^a E_T data are from refs. 20 - 22.^b Error, $\pm 10\%$.

be noted that the rate constants we have obtained for the quenching of DPB triplet by azulene and ferrocene are in good agreement with those reported by Görner [16], although our k_q^T value (5.0×10^9 M⁻¹ s⁻¹) for oxygen quenching in benzene is higher than that reported (3.7×10^9 M⁻¹ s⁻¹) by him [16].

We have also examined the quenching behaviors of DPB and ANT triplets toward some of the quenchers in ethylene glycol. The data are summarized in Table 2. Primarily as a consequence of increased viscosity, the quenching rate constants in ethylene glycol are, in general, substantially smaller than in benzene (by an order of magnitude in most cases). Surprisingly, the large relative difference in the k_q^T values observed between ANT and DPB with ferrocene as the quencher in benzene (Table 1) disappears when the solvent is ethylene glycol (Table 2). To establish whether this is due to a preferential charge transfer interaction in the case of DPB on going from a non-polar solvent (benzene) to a polar solvent (ethylene glycol), we

TABLE 2

Rate constants for the quenching of anthracene and 1,4-diphenyl-1,3-butadiene triplets in ethylene glycol

Quencher	k_q^T ^a (M ⁻¹ s ⁻¹) for the following triplets	
	ANT	DPB
Azulene	6.6×10^8	3.8×10^8
Ferrocene	4.7×10^8	4.6×10^8
Oxygen	1.5×10^8 ^b	2.1×10^8 ^b
DTBN	1.8×10^6	5.7×10^7

^a Error, $\pm 10\%$.^b Based on an assumed concentration of 2×10^{-3} M for oxygen in air-saturated ethylene glycol.

have determined the k_q^T values for ANT and DPB triplets for quenching by ferrocene in methanol; the observed values are $6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Both of these rate constants are about 50% greater than those in benzene; however, there is no significant preferential enhancement in k_q^T for DPB triplet relative to ANT triplet on going from benzene to methanol.

4. Discussion

It is evident from the data in Table 1 that azulene ($E_T = 39 \text{ kcal mol}^{-1}$ [23]) and ferrocene ($E_T = 38 - 41 \text{ kcal mol}^{-1}$ [23]) quench DPB triplet at a much slower rate than they do the three aromatic triplets, namely ANT, 1-chloroanthracene and 3,4-benzopyrene with E_T values ($40.9 - 42.5 \text{ kcal mol}^{-1}$) close to the spectroscopic triplet energy of DPB ($42.3 \text{ kcal mol}^{-1}$, from $T_1 \leftarrow S_0$ absorption in chloroform [13]). In addition to the uncertainty in the E_T values arising from a solvent effect, we recognize that, for these sensitizer triplets, azulene and ferrocene quenching corresponds to the onset of bending from the limit of diffusion-controlled energy transfer (for triplet substrates with higher E_T values). As a matter of fact, on lowering E_T by 1 kcal mol^{-1} by going from 3,4-benzopyrene to DPA, the rate constants for both azulene and ferrocene quenching are found to drop quite sharply (Table 1). To settle whether the difference in the quenching behavior of DPB triplet toward azulene and ferrocene from that of ANT or 3,4-benzopyrene is significant enough, we have used a quencher of much lower triplet energy, namely perylene ($E_T = 35 \text{ kcal mol}^{-1}$ [20]). The data in Table 1 show that the difference in the quenching rate constants of DPB and ANT or 3,4-benzopyrene triplets is retained with perylene as the quencher.

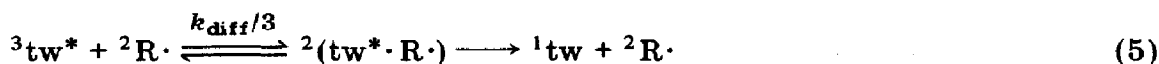
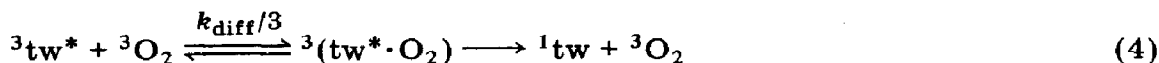
A tentative but plausible explanation for the observed departure of the quenching behaviors of DPB triplet from those of aromatic triplets of similar spectroscopic triplet energies can be sought in terms of the equilibrium



between a planar form (transoid, ${}^3\text{tr}^*$) of the diene triplet and a form (${}^3\text{tw}^*$) in which it is twisted about one of the "double" bonds. This is by analogy with stilbenes and related olefins [5, 6]. In contrast with stilbene, the quantum yield of triplet-sensitized photoisomerization of DPB is reportedly [16] very small (less than 0.05 in benzene). Thus, it is probable[†] that the minimum in the potential energy surface of DPB triplet occurs at an angle of twisting of less than 90° . The relatively low k_q^T values for azulene, ferrocene and perylene quenching of DPB triplet become explainable by the fact that the twisted form is not quenched by these quenchers because of a low vertical T_1-S_0 gap for this geometry. In contrast, the relatively high k_q^T values

[†]The authors are grateful to the referee for drawing their attention to this aspect.

for oxygen and DTBN quenching of DPB triplet are attributable to an enhanced intersystem crossing via spin exchange [24] at the perpendicular geometry (because of a favorable Franck-Condon overlap):



where $\text{R} \cdot$ denotes a stable free radical. On the assumption that the equilibrium represented by eqn. (3) is maintained fast between ${}^3\text{tr}^*$ and ${}^3\text{tw}^*$ during the triplet decay in the presence and in the absence of quenching, the following expressions for the observed triplet lifetime and the bimolecular quenching rate constant can be derived:

$$\tau_{\text{T}}^{-1} = \frac{k_{\text{d, tr}} + Kk_{\text{d, tw}}}{1 + K} \quad (6a)$$

$$k_{\text{q}}^{\text{T}} = \frac{k_{\text{q, tr}}^{\text{T}} + Kk_{\text{q, tw}}^{\text{T}}}{1 + K} \quad (6b)$$

where the subscripts tr and tw refer to transoid and twisted configurations respectively. Assuming that for the quenching of DPB triplet by perylene $k_{\text{q, tw}}^{\text{T}} \approx 0$ and $k_{\text{q, tr}}^{\text{T}}$ equals the corresponding quenching constant ($4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) for 3,4-benzopyrene, we estimate K to be 0.6 (in benzene). On the basis of this value of K and the approximation $k_{\text{d, tr}} \ll k_{\text{d, tw}}$, we calculate the rate constant $k_{\text{d, tw}}$ for intersystem crossing for the non-planar geometry to be $1 \times 10^6 \text{ s}^{-1}$ in benzene (using the observed triplet lifetime of $2.6 \mu\text{s}$). It should be noted that the values of both K and $k_{\text{d, tw}}$ for DPB are smaller than those for stilbene [5] by one order of magnitude. This suggests a pronounced decreasing trend in both the relative importance and the intersystem crossing rate of the twisted forms with increases in the polyene chain length.

On the basis of the similarity in the E_{T} values, it seems reasonable to assume that the rate constants for the quenching of the transoid form of DPB triplet by oxygen and DTBN are not different from those for the quenching of 3,4-benzopyrene. Then, using the data in Table 1, we obtain $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $k_{\text{q, tw}}^{\text{T}}$ for quenching by oxygen and DTBN respectively. It should be noted that the former rate constant is close to one-third of the diffusion-controlled rate, as expected for catalyzed intersystem crossing via spin exchange (eqn. (4)).

The fact that the relative decrease in k_{q}^{T} of DPB triplet quenching by ferrocene on changing solvent from benzene to ethylene glycol is much smaller than the tenfold decrease observed for ANT triplet suggests that in ethylene glycol the planar form (${}^3\text{tr}^*$) of the diene triplet is favored, *i.e.* the value of K is smaller. It should be noted that K for the stilbene triplet drops [5] from 8 to 2.4 on going from benzene to *tert*-butyl alcohol. The azulene

and oxygen quenching data for ANT and DPB in ethylene glycol also show the same behavior, but less strikingly. DTBN quenching in ethylene glycol, however, shows the opposite trend to that of oxygen quenching, suggesting that the effect of a smaller value of K in ethylene glycol is possibly compensated for by a decrease in $k_{q, tw}$, smaller in magnitude than that effected by the viscosity change.

As an alternative to the interpretation based on the ${}^3tr^* \rightleftharpoons {}^3tw^*$ equilibrium, the involvement of a single diene triplet (relaxed) with slightly distorted geometry may be invoked. The smaller k_q^T value for azulene and ferrocene quenching becomes explainable if the effective E_T value for this relaxed triplet is smaller than the spectroscopically observed value. Also, the higher k_q^T value for oxygen and DTBN quenching may be ascribed to polyene torsional motions in the light of the theory of Englman and Jortner [25, 26] for radiationless transitions involving displaced harmonic oscillators (the strong coupling limit). On the basis of the fact that the quenching by perylene is nearly as differentiating as that by azulene for triplets of DPB compared with ANT or 3,4-benzopyrene, we are inclined to favor the model based on the ${}^3tr^* \rightleftharpoons {}^3tw^*$ equilibrium for the diene.

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