

THE TRIPLET STATE IN STILBENE *cis-trans* PHOTOISOMERIZATION

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ABSTRACT

Stilbene triplets are further characterized by their interaction with quenchers. A previously proposed model for stilbene triplet decay and quenching, together with rate constants for excitation transfer from indeno[2,1-*a*]indene triplets to azulene, is used to account for the temperature dependence of the azulene effect on stilbene photoisomerization and is shown to lead to erroneous predictions concerning the lifetime and geometry of stilbene triplets. This conclusion is based on oxygen quenching experiments suggesting a twisted geometry for stilbene triplets in benzene solution with a lifetime of ~ 120 ns at 30° .

Azulene quenching experiments show that bromine substitution at the para position of stilbene markedly increases $^1S \rightarrow T$ intersystem crossing efficiency while substitution at the meta position does not enhance this process at 30° . These results are consistent with the fact that in contrast to the para position, the meta position is a near node in the highest occupied and lowest unoccupied molecular orbitals of stilbene.

INTRODUCTION

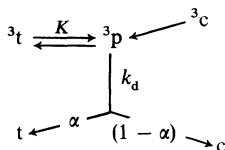
The geometry, lifetime and reactivity of stilbene triplets have to a large measure been inferred from experiments in which the stilbenes function as acceptors or donors of triplet excitation¹⁻³. Such approaches will be the subject of the first part of this paper. Knowledge concerning the efficiency of stilbene triplet interactions with a variety of quenchers has been used in determining the extent to which these triplets participate in photoisomerization following direct stilbene excitation¹⁻⁶. In the second part of this paper quenching methods will be applied in determining whether bromine atom substitution influences the efficiency of intersystem crossing in the stilbenes.

THE LIFETIME AND GEOMETRY OF STILBENE TRIPLETS IN SOLUTION

The interaction of stilbene triplets with quenchers

Under triplet (sensitized) excitation conditions stilbene photoisomerization has been proposed to occur by decay from twisted triplets, $^3p^{1-3,7}$, which lie lower in energy than cisoid triplets but are nearly isoenergetic with transoid

triplets, *Scheme 1*^{1,3}. The mechanism in *Scheme 1* is based in large part on the different responses of the two stilbene isomers as triplet excitation acceptors to changes in the triplet energy of the donor. *trans*-Stilbene behaves as a classical triplet excitation acceptor, i.e. when a donor triplet has insufficient energy to promote *t* to ³*t* the decrease in the rate constant for energy transfer, *k*_{et}, can



Scheme 1. Mechanism for stilbene triplet decay

be accounted for by assuming that the electronic energy deficiency, ΔE_T , is supplied as an activation energy (equation 1). This suggests that the transoid

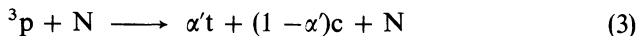
$$\Delta \ln k_{et} = - (\Delta E_T)/RT \quad (1)$$

geometry is at least close to an energy minimum in the triplet state potential energy surface. In contrast, when *cis*-stilbene is the acceptor, excitation transfer rate constants are much larger than predicted by equation 1 suggesting significant stabilization in the excited state surface as the molecule twists from cisoid geometries towards ³*p*⁰. This feature of the mechanism explains the inability of molecules with $E_T \gtrsim 57$ kcal/mol (the spectroscopic 'vertical' triplet excitation energy of *cis*-stilbene) to intercept cisoid triplets³. On the other hand the presence of transoid triplets in equilibrium with twisted triplets is suggested by the observation that addition of quenchers having low lying triplets, $E_T \lesssim 48$ kcal/mol, leads to increased *trans/cis* photostationary ratios, ($[t]/[c]$)_s,



presumably due to interaction with transoid triplets (equation 2) whose spectroscopic triplet excitation energy is 49 ± 1 kcal/mol^{1,3}.

A second quencher type appears to interact with ³*p*. Only one quencher of this type has been reported in the case of stilbenes, di-*tert*-butyl nitroxide, N, and its presence has been shown to produce a modest increase in ($[c]/[t]$)_s



(equation 3, $\alpha/\alpha' = 1.11$)¹². It has been suggested that electron spin exchange with the radical quencher causes vibrational relaxation of the stilbene triplet to the ground state vibrational manifold¹².

Several versions of potential energy curves for twisting about the central bond in the triplet state of stilbene have been proposed all of which adhere to the requirements of *Scheme 1*. The differences are in the description of the energetics for twisting from ³*t* to ³*p*. Three possibilities have been considered, the first two having energy minima at ³*t* and ³*p* with ³*t* lower^{2,3} or higher¹ in

energy than 3p , and the third, having a single energy minimum at 3t with 3p somewhat higher in energy^{11,13}. A fourth possibility which was not meant to account for the results which led to *Scheme 1* has 3p significantly lower than either 3t or 3c and is based on molecular orbital calculations^{14,15}.

In the following a study of the interaction of stilbene triplets with quenchers will be described which was intended to provide insight concerning the relative energies of 3t and 3p . The question whether 3p is higher or lower in energy than 3t is crucial since the answer may provide information bearing on the more important question of whether ground state and triplet energy surfaces touch, cross or avoid crossing at a twisted geometry. It should be noted that with respect to *trans* ground state molecules the best estimate of the energy content of 3t is 49 ± 1 kcal/mol while that of the twisted transition state for thermal *cis-trans* isomerization is 48 ± 2 kcal/mol¹.

1. The azulene effect

We start by adopting the mechanism in *Scheme 1* for sensitized stilbene photoisomerization. Using benzophenone as the sensitizer ($E_T = 68$ kcal/mol)¹⁹, azulene as the quencher ($E_T = 30$ kcal/mol)²⁰, and including equation 1 in the mechanism ($k_q = k_{az}$), k_{az}/Kk_d ratios can be obtained either from the response of $([t]/[c])_s$ to azulene concentration (equation 4), where k_c and

$$\left(\frac{[t]}{[c]}\right)_s = \frac{k_c}{k_t} \frac{\alpha}{1 - \alpha} \left(1 + \frac{k_{az}[Az]}{\alpha Kk_d}\right) \quad (4)$$

k_t are rate constants for triplet excitation transfer from benzophenone to *cis*- and *trans*-stilbene, respectively⁴, or from the response of isomerization quantum yields to azulene (equation 5)²¹. The additional azulene effects of

$$\phi_{t \rightarrow c} = (1 - \alpha) \left(1 + \frac{k_{az}[Az]}{Kk_d}\right) \quad (5)$$

internal filtering and quenching of sensitizer triplets do not affect stationary states, and are compensated for in the quantum yield measurements by employing actinometry solutions in which *trans*-1,2-diphenylpropene whose triplets are not quenched by azulene³, is substituted for stilbene²¹. Use of either equation 4 or 5 has been found to give identical k_{az}/Kk_d ratios within experimental uncertainty. The sensitivity of k_{az}/Kk_d to solvent viscosity has played an important role in supporting the notion that intersystem crossing is not a significant decay path when the stilbenes are excited by direct light absorption⁴. Values for these ratios obtained in different solvents at 30° are shown in *Table 1* along with corresponding solvent viscosities. It can be seen that in aprotic solvents the ratios are to a good approximation inversely proportional to solvent viscosity, *Figure 1*, as would be expected if k_{az} were diffusion-controlled and Kk_d were solvent independent. In agreement with observations by Liu using anthracenes as quenchers²² and by Whitten and Lee using azastilbenes as the donors²¹ anomalously large k_{az}/Kk_d values are obtained in alcoholic media. It has been reasoned that if k_{az} is diffusion controlled in the more fluid solvents it must surely be diffusion controlled in as viscous

Table 1. Values of k_{az}/Kk_d at 30°.

Solvent	$k_{az}/Kk_d, M^{-1}$	η, cP
<i>n</i> -Pentane	112	0.220
Acetonitrile	88	0.329
Toluene	59	0.526
Benzene	51	0.561
Methanol	106	0.510
<i>tert</i> -Butyl alcohol	85	3.316

a solvent as *tert*-butyl alcohol²⁴ and the large k_{az}/Kk_d was tentatively attributed to a marked increase (ninefold in *tert*-butyl alcohol)⁴ in the effective lifetime of stilbene triplets, $(Kk_d)^{-1}$ in alcoholic solvents^{4, 15}.

The azulene effect in several solvents has been measured at different temperatures using a miniature merry-go-round apparatus which was initially employed in diene photoisomerization studies²⁵. Whitten and Lee's quantum yield method (equation 4)²¹ was used primarily in this work because it

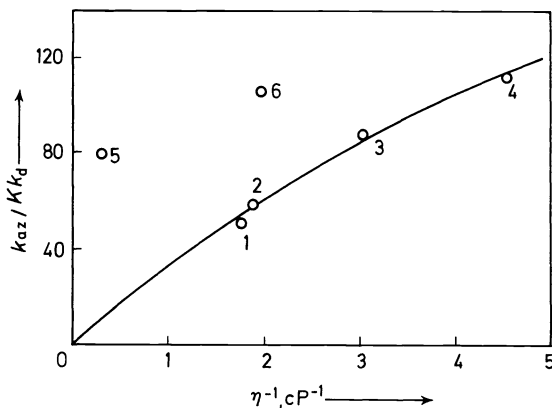


Figure 1. The variation of k_{az}/Kk_d with η^{-1} at 30°. Solvents are: benzene 1, toluene 2, acetonitrile 3, *n*-pentane 4, *tert*-butyl alcohol 5, methanol 6.

requires shorter irradiation times. Observations in toluene and *tert*-butyl alcohol, expressed as k_{az}/Kk_d ratios, are plotted versus T/η in Figure 2²⁶. Observations in *n*-pentane and acetonitrile give similar but different curves. The non-linearity of these plots and the fact that data for different solvents fall on different curves appear to suggest that k_{az} is not the only temperature and solvent dependent quantity but that the effective stilbene triplet lifetime also depends on these variables. The efficiency of exothermic triplet excitation transfer in solution is usually assumed to be diffusion-controlled following a

$$k_{dif} = 8RT/2000\eta \quad (6)$$

modified Debye equation (equation 6)²⁷. The temperature dependence of stilbene triplet decay rate constants might be extracted from data of the type shown in Figure 2 by assuming $k_{az} = k_{dif}$ and applying equation 6. However, evidence has been presented which suggests that in the less

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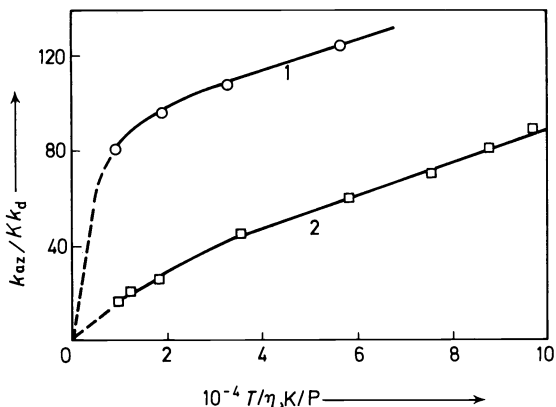
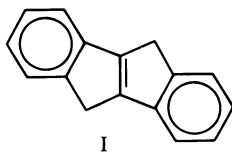


Figure 2. The variation of k_{az}/Kk_d with T/η in *tert*-butyl alcohol (curve 1) and toluene (curve 2).

viscous hydrocarbon solvents usually employed in photochemical studies rates of exothermic triplet excitation transfer can be slower than rates of diffusion^{24,28}. It seems desirable, therefore, to have an empirical measure of the T/η dependence of k_{az} instead of relying as before^{1,4} on the Debye equation. Since stilbene triplets are too short-lived to allow their detection by conventional flash-kinetic spectroscopy we have used the rigid stilbene analogue indeno[2,1-a]indene, I, as a model for transoid stilbene triplets (equation 7).



I



2. The T/η dependence of k_i

Flash kinetic determination of k_i values has been carried out using a Northern-Precision kinetic flash-photolysis apparatus²⁹. Following measurement of the decay characteristics of I triplets, an azulene solution is admitted into the cell via a breakseal and the lifetime of I triplets is measured again. Triple-jacketed cells similar to that described by Jackson and Livingston³⁰ were used which allow temperature control by circulation of a transparent liquid (methanol) through the outer jacket. Transient decays were primarily first-order, but second-order decay components were exactly corrected for by using the integrated expression for mixed first- and second-order triplet decay³¹ in conjunction with a general least-squares computer programme developed by DeTar³². The rate constants fall into two main categories. Linear dependence of k_i on T/η is observed in toluene and *n*-pentane and non-linear dependence of k_i on T/η is observed in *tert*-butyl alcohol and acetonitrile. The results of the studies in toluene and *tert*-butyl alcohol which are more complete are plotted in Figure 3. Also shown in Figure 3 is the

behaviour predicted by the modified Debye equation (equation 6). The fact that linearity is maintained throughout the T/η range in toluene suggests strongly that k_i is diffusion-controlled in this solvent. The experimental values are somewhat smaller than those predicted by equation 6, falling in-

$$k_i = 8RT/3750\eta \quad (8)$$

stead on a line described by equation 8. In contrast k_i values in *tert*-butyl alcohol are larger than those predicted by equation 6. This is consistent with other observations which suggest that diffusion coefficients in alcohols are double those predicted by the Stokes-Einstein equation upon which equation 6 is based³³.

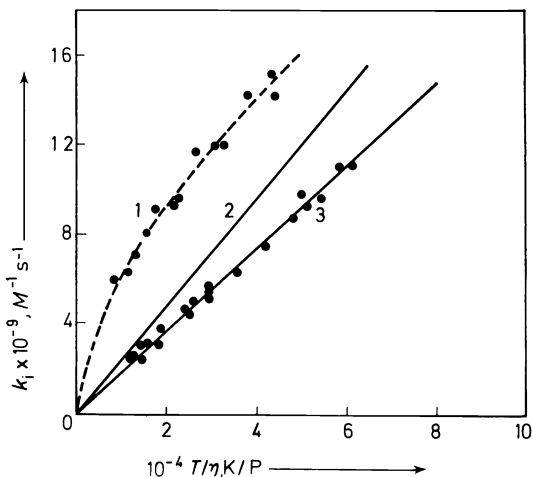


Figure 3. The variation of k_i with T/η in *tert*-butyl alcohol (curve 1) and toluene (line 3). The behaviour predicted by equation 6 is shown by line 2.

Before applying the above rate constants to the interpretation of the stilbene-azulene data it is of interest to consider these different variations of k_i with T/η in toluene and *tert*-butyl alcohol. Non-linearity of the type exhibited by the *tert*-butyl alcohol results in Figure 3 has been attributed to a decrease of the rate constants for exothermic triplet excitation transfer below those expected for a diffusion-controlled process as the viscosity of the medium drops below 3 cP²⁴. Thus, the curved line could simply reflect a large fraction of ineffective indeno[2,1-a]indene triplet-azulene encounters at the higher temperatures. This possibility seems unattractive for two reasons. First, more pronounced curvature, instead of linearity, would be expected in toluene where much lower viscosities are attained and secondly, most of the observed rate constants in *tert*-butyl alcohol are larger than would be predicted even if the left hand side of equation 5 were multiplied by two. Another possibility which also seems remote can be considered. Based on its absorption spectrum³⁴ and the weak emission spectra which were recently reported²⁰, the lowest azulene triplet and singlet excitation energies are 30 and 39 kcal/mol, respectively. Both of these are substantially lower than the *trans*-stilbene

triplet energy and triplet-singlet excitation transfer by dipole-dipole interaction could in principle compete with diffusion-controlled triplet-triplet excitation transfer. While triplet-singlet excitation transfer is not usually observed in solution its occurrence has been proposed in the benzophenone-*perylene* system^{35,36} and in the acetone-9,10-dibromoanthracene system, where the presence of the heavy atom substituents appears to be crucial^{37,38}. An important criterion for establishing the dipole-dipole nature of the excitation transfer process in the benzophenone-*perylene* system was the finding³⁶ that in agreement with theory³⁹, the probability of transfer is proportional to $(T/\eta)^{\frac{1}{2}}$. Interestingly, a plot of k_i in *tert*-butyl alcohol versus $(T/\eta)^{\frac{1}{2}}$ is linear, possibly suggesting that triplet-singlet excitation transfer is the dominant process in this solvent. If this possibility is tentatively accepted the data in *Figure 3* suggest that the nature of the interaction between I and azulene is solvent dependent resulting in triplet-triplet energy transfer in toluene and triplet-singlet energy transfer in *tert*-butyl alcohol. This conclusion would render the claim that triplet-singlet excitation transfer does not occur in the benzophenone-*perylene* system³⁹ less secure since the $(T/\eta)^{\frac{1}{2}}$ dependence was observed in trichlorotrifluoroethane³⁶, while the absence of the dipole-dipole interaction is claimed for benzene solutions⁴⁰. Since the $S^1 \leftarrow S^0$ transition in azulene is rather weak³⁴ the notion of triplet-singlet excitation transfer in our system does not seem very attractive and we are investigating the third possibility that the curvature of the *tert*-butyl alcohol data in *Figure 3* reflects a small but real deviation from the theoretical prediction of equation 6 for diffusion-controlled triplet excitation transfer.

3. Use of k_i values in the (mis)interpretation of the azulene-stilbene observations

A single triplet excitation transfer rate constant from a stilbene to azulene has been measured directly. The donor was 4-nitro-4'-methoxystilbene, nanosecond laser flash-kinetic spectroscopy was employed and the measurement was made in benzene at room temperature⁵. The value of $k_{az} = 6.0 \times 10^9 M^{-1} s^{-1}$ observed in this system is comfortably close to our value of $k_1 = 6.7 \times 10^9 M^{-1} s^{-1}$ measured in benzene at 23°C⁴¹, suggesting that substitution of the k_i values for k_{az} in the k_{az}/Kk_d ratios should give the temperature dependence of Kk_d . Thusly lulled into a false security we proceed to calculate effective stilbene triplet lifetimes, $(Kk_d)^{-1}$, ranging from 4.8–8.7 ns in toluene (+70° to –50°) and from 7.7–14.4 ns in *tert*-butyl alcohol (80° to 30°). While the variations in Kk_d could be due in part to activation energies associated with k_d , the rate constant for intersystem crossing from 3p , there are instances where reasonable interpretations of data are obtained by assuming that $^1S \rightarrow T$ or $^1T \rightarrow S$ intersystem crossing rate constants are temperature independent^{25,42,43}. Tentatively assigning the temperature dependence in Kk_d entirely to changes in K and substituting the thermodynamic relationship for the equilibrium constant gives equation 9, where

$$\log k_d K = -\frac{\Delta H}{2.303 RT} + \frac{\Delta S}{2.303 R} + \log k_d \quad (9)$$

ΔH and ΔS are the enthalpy and entropy differences between 3t and 3p . Plots of the toluene and *tert*-butyl alcohol data, *Figure 4*, show satisfactory adherence to equation 9, giving ΔH values in the two solvents of 0.8 and

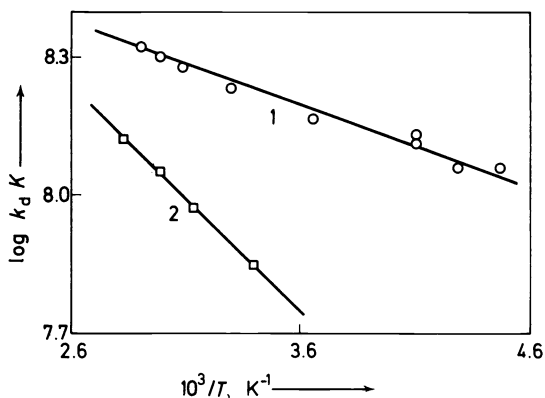


Figure 4. The temperature dependence of estimated $k_d K$ values in toluene (line 1) and in *tert*-butyl alcohol (line 2).

2.7 kcal/mol, respectively. The implication is that twisted triplets lie somewhat higher in energy than transoid triplets and that the energy difference is larger in *tert*-butyl alcohol. Consistent application of the model suggests further than the abnormally high k_{az}/Kk_d ratios in *tert*-butyl alcohol can be attributed in part to a decrease in the equilibrium constant K which overpowers a substantial increase in k_d suggested by the intercepts of the lines in Figure 4.

4. The quenching of 3p , or the fly in the ointment

A plausible interpretation of data has been presented indicating a transoid preferred geometry for stilbene triplets in solution. However, in contrast to azulene and several other quenchers which appear to deactivate 3t during the excitation transfer process causing more stilbene triplets to decay to the *trans* isomer (equation 2)¹, use of di-*tert*-butyl nitroxide has been shown to reduce stilbene triplet lifetimes, modestly favouring decay to the *cis* isomer during the deactivation process (equation 3)¹². To account for the apparent anomaly of quenching of transoid triplets in some cases and of twisted triplets in another it was initially suggested that the free radical quencher forms a complex with stilbene triplets in which 3p geometries are more favoured than normal^{12a}. This proposal was later abandoned in favour of the suggestion that the radical interacts particularly efficiently with stilbene triplets because the $^1T-^0S$ energy gap is very small at the equilibrium geometry (presumably 3p) of the triplet^{12b}. This suggestion is obviously in conflict with the interpretation of the temperature dependence of the azulene effect given above. It must nonetheless be given serious consideration since it can be reasonably argued that the availability of an exchange quenching mechanism not involving triplet excitation transfer allows di-*tert*-butyl nitroxide to interact with stilbene triplets in their preferred twisted geometry while azulene and other triplet excitation acceptors can interact with stilbene triplets only when large electronic $^1T-^0S$ energy gaps are achieved in transoid configurations.

There are two other reasons for concern regarding the validity of the

assumptions made in the preceding section. First, substitution of k_1 for k_{az} leads to predicted stilbene triplet lifetimes approximately an order of magnitude shorter than the lifetime of a weak transient absorption at 360 nm observed in benzene solutions of *trans*-stilbene following excitation with a radiolysis pulse of 25 ns duration⁴⁴. This transient has been assigned to stilbene triplets and its lifetime (110 ± 10 ns at room temperature) is in good agreement with lifetimes determined by laser flash-kinetic spectroscopy for several nitrostilbene triplets⁵. Secondly, the efficient quenching of nitrostilbene triplets by oxygen has been measured directly and has been found not to alter $([t]/[c])_s$ for these stilbenes^{5,6}. Prompted by these observations we have examined the effect of oxygen on the photoisomerization of the stilbenes⁴⁵. The results account for the lifetime discrepancy and require modification of the stilbene triplet decay and quenching mechanisms shown in *Scheme 1* and equation 2.

5. The oxygen effect

Photostationary *trans/cis* stilbene compositions were determined for the benzophenone-sensitized photoisomerization in benzene and *tert*-butyl alcohol as a function of azulene concentration in degassed solution and in the presence of air and oxygen. Excitation was at 366 nm at 30° and analyses were by g.l.p.c. as previously described². Air or oxygen were solvent saturated and bubbled through the irradiated solutions. The same results were obtained for solutions which were open to the air and solutions through which a constant air flow was maintained. No significant changes in azulene concentration were detected by u.v. analyses. As for degassed solutions plots of $([t]/[c])_s$ ratios obtained in the presence of oxygen versus azulene are linear with the only difference being a strong attenuating oxygen effect on the

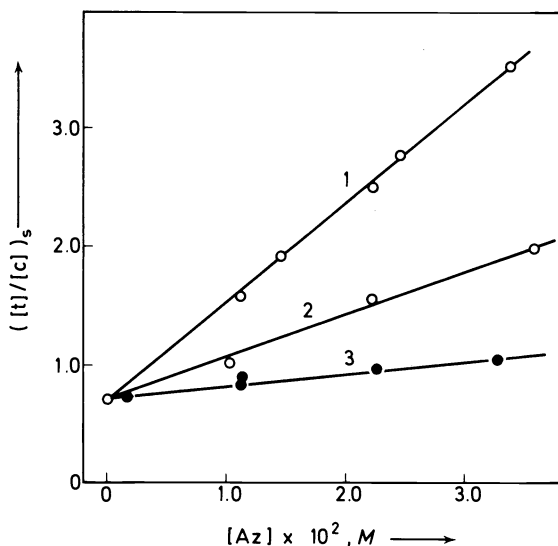


Figure 5. The effect of azulene on the benzophenone-sensitized photoisomerization of the stilbenes at 30° in benzene: degassed, line 1; in the presence of air, line 2; in the presence of oxygen, line 3.

Table 2. Attenuation of the azulene effect by oxygen alcohol

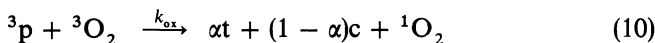
Conditions	Benzene			<i>tert</i> -Butyl alcohol		
	<i>r</i>	<i>i</i>	[O ₂], M × 10 ³ †	<i>r</i>	<i>i</i>	[O ₂], M × 10 ³ ‡
Degassed	120	0.69	0	201	0.77	0
Air	51	0.70	1.6 ₂	80	0.71	1.7
O ₂	15	0.70	7.7 ₄	35	0.69	8.0

† J. E. Jolley and J. H. Hildebrand, *J. Amer. Chem. Soc.* **80**, 1050 (1957).

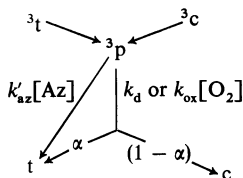
‡ Estimated from data for other alcohols in F. Fischer and G. Pfeleiderer, *Z. anorg. Chem.* **124**, 61 (1922), cf. J. Livingston, R. Morgan and H. R. Pyne, *J. Phys. Chem.* **34**, 2045 (1930).

slopes of the lines. Data obtained in benzene are plotted in *Figure 5*. Slope/intercept ratios, *r*, and the intercepts, *i*, of the lines are shown in *Table 2*.

The oxygen attenuation effect on the slope of the azulene plots suggests strongly that oxygen interacts with stilbene triplets, thereby decreasing their lifetime. The common intercepts of the sets of lines in each solvent show that the oxygen quenching interaction does not alter the *trans/cis* decay ratio of the quenched stilbene triplet. The simplest explanation for this result is that oxygen interacts with twisted triplets as shown in non-vertical quenching step



10. A close analogy for this process is provided by the quantum chain carrying step in the photoisomerization of 1,3-dienes^{46,47}. Since oxygen should also be an efficient quencher of transoid triplets, the important conclusion is that almost all stilbene triplets must be present in twisted geometries in solution. It follows that, contrary to the mechanism assumed above (equation 2), the azulene effect must also have its origin in the interaction of twisted triplets with azulene. These conclusions are incorporated in the mechanism shown in *Scheme 2*.



Scheme 2. Modified mechanism for stilbene triplet decay and interaction with quenchers

Accordingly, equation 4 is replaced by photostationary expression 11. The

$$([t]/[c])_s = (k_c/k_t) \left(\frac{\alpha}{1 - \alpha} \right) \left(1 + \frac{k'_{\text{az}}[\text{AZ}]}{\alpha(k_d + k_{\text{ox}}[\text{O}_2])} \right) \quad (11)$$

lifetime of stilbene triplets, now expressed as $\tau = k_d^{-1}$, can be estimated from the slope/intercept ratios in *Table 2* using equation 12, where r_0 is the

$$\tau = (r_0 - r)/rk_{\text{ox}}[\text{O}_2] \quad (12)$$

slope/intercept ratio for degassed solutions. Using the benzene data in Table 2 and assuming $k_{ox} = 7.0 \times 10^9 M^{-1} s^{-1}$, the known value of the rate constant for *p*-nitrostilbene quenching by oxygen^{5,6}, values for τ of 119 and 129 ns are obtained from air-saturated and oxygen-saturated experiments, respectively. These lifetimes are in excellent agreement with the values obtained in the pulse radiolysis experiments⁴⁴, and since $k_{az} = \alpha r_0/\tau$ they give $k_{az} \approx 4.0 \times 10^8 M^{-1} s^{-1}$, well below the corresponding value of k_i . The *tert*-butyl alcohol data cannot be interpreted quantitatively since neither k_{ox} nor $[O_2]$ is known in this solvent. Reasonable estimations of these quantities give $\tau = 200 \pm 40$ ns at 30° suggesting that the large r_0 observed is not due primarily to an increase in stilbene triplet lifetime as had been previously suggested^{4,21-23}, but to a larger k'_{az} .

The unsuitability of indeno[2,1-a]indene as a model for stilbene triplets provides further support for marked departure of the equilibrium conformation of stilbene triplets from transoid geometry. A corollary to this proposition is the conclusion that in its quenching interaction di-*tert*-butyl nitroxide¹² provides a much better probe for the geometry of unperturbed stilbene triplets than does azulene. Upward revision of the stilbene triplet lifetime to $\tau \approx 120$ ns allows re-evaluation of the rate constant k_n for this process in benzene. Inclusion of equation 3 in Scheme 2 leads to photostationary expression 13. From

$$([c]/[t])_s = (k_i/k_c) \left(\frac{(1 - \alpha) + (1 - \alpha') k_n \tau [N]}{\alpha + \alpha' k_n \tau [N]} \right) \quad (13)$$

equation 13 and the data in reference 12 a value of $k_n \tau \approx 110 \pm 20 M^{-1}$ (equivalent to the value of $k_n \tau \alpha'/\alpha = 100 \pm 20$ given in reference 12a) is obtained from which $k_n \approx 9 \times 10^8 M^{-1} s^{-1}$ can be calculated. This rate constant is not much larger than estimated rate constants for the quenching of rigid planar aromatic hydrocarbon triplets by N (compare with $k = 6.4 \times 10^8 M^{-1} s^{-1}$ ^{12b,48} for phenanthrene triplet quenching) and suggests that the efficiency of di-*tert*-butyl nitroxide quenching interactions is not very sensitive to the geometry of the quenched triplet as had been supposed.

6. Reinterpretation of the azulene effect

Although as proposed in Scheme 2 the azulene effect probably has its origin in the interaction of ³p triplets with azulene a more detailed mechanism is required in order to account for (1) strong dependence of k'_{az} on solvent viscosity as indicated by the data in Table 1 despite the fact that $k'_{az} < 0.1 k_{dif}$ in benzene, (2) the fact that the quenching interaction gives only *trans* ground state molecules, and (3) the observation of $k'_{az} \approx k_{dif}$ for 4-nitro-4'-methoxystilbene although oxygen experiments indicate a twisted equilibrium geometry for this stilbene also^{5,6}. Such an interpretation of the azulene effect is given in equations 14-16, where brackets designate exciplexes or



encounter complexes. It follows that k'_{az} in equation 11 is replaced by the expression in equation 17, which reduces to equation 18 if it is assumed that

$$k'_{az} = \frac{k_{14}K_{15}(k_{16}/k_{-14})}{(k_{16}K_{15}/k_{-14}) + k_{16}/k_{-15} + 1} \quad (17)$$

$$k'_{az} = k_{dif}K_{15}/(1 + K_{15}) \quad (18)$$

k_{14} , k_{-14} , k_{16} are diffusion-controlled, and that equilibration step 15 is faster than diffusional separation of the donor-acceptor pair. Examination of equation 18 shows that the proposed mechanism accounts for the strong dependence of $k'_{az}\tau$ values on solvent viscosity (Table I). It is important to note here that the alternative mechanism in which step 15 is the rate-determining process leading to excitation transfer, i.e. $k_{-15} = 0$, predicts k'_{az} to be approximately proportional to k_{15} thus failing to predict solvent viscosity dependence for k'_{az} .

A value of $K_{15} \approx 0.04$ at 30° in benzene can be calculated using equation 18 by assuming $\tau = 120$ ns and $k_{dif} = 10^{10} M^{-1} s^{-1}$ (see toluene data in Figure 3, $T/\eta = 5.4 \times 10^4$ K/P). An approximate value of $K_{15} \approx 0.1$ at 30° can be calculated from the *tert*-butyl alcohol data possibly suggesting a somewhat larger stability for the azulene-³t complex in the more polar solvent. It can also be seen from equation 18 that k'_{az} will approach k_{dif} in systems for which K_{15} is large (e.g. > 5). It appears that 4-nitro-4'-methoxystilbene represents such a system and it is possible to imagine that in an exciplex intermediate between the triplet state of this polar stilbene molecule and a planar acceptor like azulene more stabilization is attained when the stilbene partner assumes nearly planar transoid geometries.

The temperature dependence of K_{15} in toluene can be estimated from the data in Figures 2 and 3 assuming that $k_i = k_{dif}$ and that the lifetime of stilbene triplets, $\tau = 120$ ns, is temperature independent in fluid solutions. A logarithmic plot of K_{15} values obtained in this way versus T^{-1} , Figure 6, gives $\Delta H_{15} = -0.81$ kcal/mol and $\Delta S_{15} = -9.1$ e.u. Since even a small tempera-

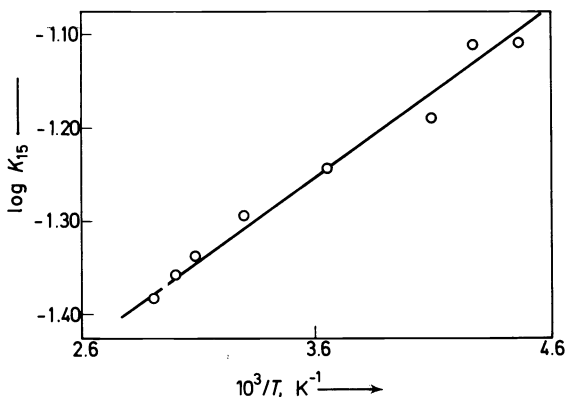


Figure 6. The temperature dependence of estimated K_{15} values in toluene.

ture dependence in τ could invalidate this analysis of the calculated K_{15} values, it is presented here primarily because it seems instructive. According to *Figure 6* the stilbene triplet–azulene pair has a higher entropy and enthalpy content when the stilbene partner assumes twisted geometries. Thus, it appears that enthalpy favours 3t geometries while entropy favours 3p geometries in the encounter complex and that entropy wins out over the entire temperature range employed in our experiments. If, furthermore, it is tentatively assumed that azulene does not greatly perturb the energetics of the $^3t \rightleftharpoons ^3p$ interconversion the same enthalpy–entropy conflict would apply to free stilbene triplets as well. This information can be crucial to the construction of potential energy curves as a function of torsional angle about the central bond, because potential energy differences are best approximated by enthalpy rather than by free energy changes. It is, therefore, quite plausible that the potential energy is lowest for the 3t geometry, as had been inferred from the functioning of the stilbenes as acceptors of triplet excitation, but that the free energy at the higher temperatures is lowest for 3p and hence the equilibrium geometry of the stilbene triplets corresponds to 3p . At lower temperatures (below 90K if we assume that ΔH_{15} and ΔS_{15} can be applied to the stilbene triplet) the enthalpy term could dominate and the equilibrium constant would then favour 3t . Blue shifts in the wavelength of the triplet–triplet absorption maxima of stilbene⁴⁴ and nitrostilbenes^{5,6} when the medium is changed from a liquid solvent (e.g. benzene at room temperature) to frozen solution (e.g. EPA or hydrocarbon glass at 77 K), have in fact been suggested to imply that the stilbene triplets are more twisted in the liquid state^{5,6,44}. Since deuterium isotope effects on the decay rate constants of stilbene triplets provide strong evidence supporting a transoid geometry in rigid media, primarily owing to a medium imposed inhibition of $^3t \rightarrow ^3p$ torsional displacement², the assignment of the blue shifts to changes in geometry is probably accurate. It would be of interest to determine whether such shifts can be observed as the temperature is lowered in media which remain fluid throughout the temperature range (e.g. isopentane or propane).

7. The energetics of twisting in the stilbene triplet state

A possible energy diagram for twisting about the central bond in the stilbene triplet state which is consistent with all presently available spectroscopic, photochemical and quenching data is proposed in *Figure 7*⁴⁹. The curve in dashed lines is based on assumed free energy differences ($\Delta F \simeq \Delta F_{15}$) and accounts for the results of stilbene triplet interactions with quenchers. The free energy minimum is purposely displaced toward the *cis* side of 90° because the natural decay ratio in solution, $\alpha/(1 - \alpha)$, favours decay to the *cis* ground state as does the quenching interaction with *tert*-butyl nitroxide. A shallow minimum at the twisted configuration is shown since the deactivation of stilbene triplets by oxygen to either ground state isomer, suggests that the 22 kcal/mol energy gap required in equation 10, provided $^1\Delta_g$ oxygen is formed, is achieved with nearly the same probability by torsional displacements towards either transoid or cisoid geometries. The dashed curve is flat towards the *trans* side and rises steeply towards the *cis* side since the larger energy gap required for excitation transfer to azulene ($E_T = 30$ kcal/mol) is apparently achieved only by torsional displacement toward

transoid geometries. In this connection we recall that stilbene triplet dynamics within donor-acceptor cages (or exciplexes) have previously been considered in discussing the interaction of the stilbenes with low triplet energy donors, $E_T \lesssim 48$ kcal/mol^{1, 16, 17}. Since in such systems the triplet energies of donor and acceptor are balanced, electronic energy may remain with either partner upon diffusive separation. The experimental observations

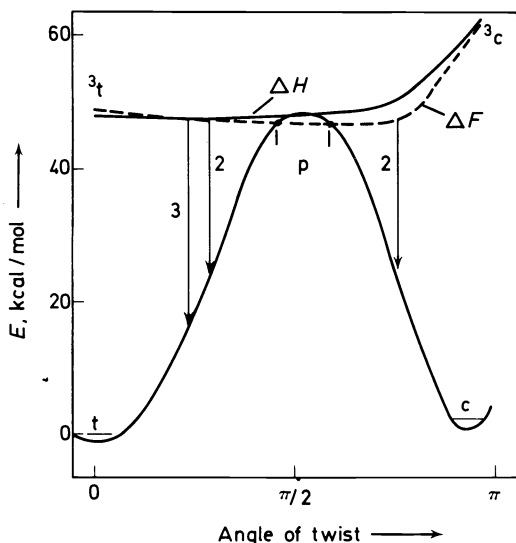


Figure 7. Possible energy diagram for twisting about the central bond of stilbene in the ground state and in the lowest triplet state (see text). The points labelled 1 may represent geometries of high natural decay probability. Lines 2 represent excitation transfer to oxygen and line 3 represents excitation transfer to azulene.

show that the excitation remains most often with the stilbene partner although the 3t to ground state donor transfer is exothermic (consider, for example, benzanthrone, $E_T \approx 46$ kcal/mol^{1, 3} or 9,10-dichloroanthracene, $E_T = 40.2$ kcal/mol¹⁶). The speculation that such results reflect a relatively long residence time for the stilbene partner of the donor-acceptor pair in 3p rather than 3t geometries¹ is clearly borne out by the present study.

Also shown in Figure 7 is a solid line for the triplet state which is tentatively based on ΔH_{15} and approximates the expected changes in potential energy as the central torsional angle is changed. This curve is consistent with the functioning of *trans*- and *cis*-stilbene as vertical and non-vertical acceptors of triplet excitation, respectively.

THE POSITIONAL DEPENDENCE OF THE HEAVY ATOM EFFECT ON BROMOSTILBENE PHOTOISOMERIZATION

Azulene quenching experiments have been used in determining the extent to which stilbene triplets participate in *cis-trans* photoisomerization following direct stilbene excitation⁴. On the basis of these experiments it has been concluded that at room temperature intersystem crossing is a negligible decay channel in the stilbenes⁴, but becomes a significant process in para

substituted stilbenes provided that the substituent is capable of enhancing intersystem crossing. We have reported preliminary observations suggesting intersystem crossing enhancement in the *p*-bromostilbenes¹, and Bent and Schulte-Frohlinde have published similar results for several *p*-nitrostilbenes^{5,6}. Since application of the azulene method as a mechanistic probe in stilbene photoisomerization has aroused some controversy^{50,51} it is important to note that by employing laser flash-kinetic spectroscopy Bent and Schulte-Frohlinde have provided direct confirmation of the validity of the method.

A substantial bromine substituent effect was revealed by comparison of the temperature dependence of fluorescence, Φ_f , and isomerization, $\Phi_{t \rightarrow c}$, $\Phi_{c \rightarrow t}$, quantum yields for the stilbenes and the *p*-halostilbenes⁵²⁻⁵⁴. Increasing the temperature in the parent hydrocarbon from -180° to 25° increases $\Phi_{t \rightarrow c}$ while decreasing Φ_f , these two processes being coupled throughout the temperature range⁵²⁻⁵⁶. In *p*-bromostilbene $\Phi_{t \rightarrow c}$ is reported to be temperature independent while Φ_f increases modestly as the temperature is decreased^{53,53}. The temperature independence of $\Phi_{c \rightarrow t}$ in the systems studied has revealed no difference in behaviour between excited *cis*-stilbene and its halogen substituted derivatives^{52,54}. However, halogen substitution, especially in the meta position, has been reported to lower $\Phi_{c \rightarrow t}$ significantly^{52,54,57} and it has been suggested that enhanced spin-orbit coupling induces very rapid $^1c \rightarrow ^3c \rightarrow ^0c$ decay^{57,58}. This suggestion contradicts the commonly expressed view^{1,6} that, with the exception of a usually minor cyclization component from 1c to dihydrophenanthrene⁵⁹ (DHP), torsion about the central bond to twisted geometries, 1p and 3p , is the major decay mode of *cis*-excited states. The low $\Phi_{c \rightarrow t}$ values were obtained by u.v. analysis of stilbene mixtures resulting from excitation with 313 nm radiation⁵⁷. Accurate measurements are difficult to make under these conditions since at this wavelength the extinction coefficients of the *trans* isomers are five to ten times larger than those of the *cis* isomers and photostationary states are generally ~ 90 per cent *cis*. Consequently, the low quantum yields could reflect analytical inaccuracy and/or failure to correct observed *trans* \rightarrow *cis* conversions for large back reaction contributions. These considerations prompted the work described in the final part of this paper.

1. Photoisomerization quantum yields

Irradiations were carried out at 30° in a merry-go-round apparatus using 313 nm light in the presence and in the absence of visible light absorbed by the DHPs. We have utilized larger stilbene concentrations in *n*-pentane and g.l.p.c. analyses and have made appropriate back-reaction corrections⁶⁰. Large *cis-trans* conversions due to bromine atom catalysis were avoided by including mossy zinc in the bottom of the irradiation ampoules⁶¹. The benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene was used for actinometry⁶⁰. Preliminary quantum yields obtained in our work⁶² are shown in Table 3 along with corresponding values reported by Krüger and Lippert⁵⁷ and Malkin and Fischer⁵². Simultaneous visible irradiation does not affect *trans* \rightarrow *cis* quantum yields but appears to increase *cis* \rightarrow *trans* quantum yields for the bromostilbenes. This wavelength effect is not fully understood and will be investigated further. It is most likely related to

excitation of DHPs which form only from the *cis* isomers. While our observations indicate a modest decrease in $\Phi_{c \rightarrow t}$ for *m,m'*-dibromostilbene, they do not show the dramatic decrease which was reported previously⁵⁷. Furthermore, Table 3 shows that we find *trans* isomers to be significant components at photostationary states obtained by exciting at 313 nm and even more so when excitation is at 254 nm where *cis* and *trans* isomers have more nearly similar extinction coefficients (e.g. for *m,m'*-dibromostilbene ϵ_c/ϵ_t is 0.157 and 1.67 at 313 and 254 nm, respectively)⁶².

Table 3. Isomerization quantum yields and photostationary compositions

Compound	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$	%[t] _s	%[t] _s †
Stilbene‡	0.52 (0.50)	0.33 (0.35)	8.3 (7)	52
<i>p</i> -Bromostilbene‡	0.54 (0.35)	0.4 (0.16)	11.0 (—)	62
<i>m</i> -Bromostilbene§	0.53 (0.46)	0.33 (0.18)	11.4 (6)	59
<i>m,m'</i> -Dibromostilbene§	0.57 (0.53)	0.22 (<0.05)	8.0 (~0)	69

† These photostationary states are attained using 254 nm excitation.

‡ Values in parentheses are from reference 52.

§ Values in parentheses are from reference 57.

The benzophenone-sensitized photoisomerizations of the stilbenes in Table 3 give nearly identical photostationary states, ~40 per cent *trans*, see Table 4, which are approached at the same rate under identical conditions. Thus, sensitized *cis* → *trans* quantum yields are not diminished by bromine substitution and the postulated rapid ³c → c decay⁵⁷ is ruled out.

Table 4. Azulene effects on photoisomerizations of stilbenes in *n*-pentane at 30°

Compound	r_d †	r_s ‡	%[t] _s §
Stilbene	14	304	37.0
<i>p</i> -Bromostilbene	31	56	39.6
<i>m</i> -Bromostilbene	12	140	45.3
<i>m,m'</i> -Dibromostilbene	23	400	37.5

† Slope/intercept ratios for excitation at 313 nm; similar results were obtained at 254 nm.

‡ Benzophenone-sensitization.

§ Photostationary states for benzophenone-sensitization in the absence of azulene, %[t]_s = 100 α.

A possible explanation for the decrease in $\Phi_{c \rightarrow t}$ under direct excitation conditions is that it does not involve heavy-atom-enhanced intersystem crossing but is due to the larger moments of inertia of the aryl groups which may tend to favour cyclization to DHP over torsional ¹c → ¹p displacement. Support for this suggestion is provided by preliminary observations which show that prolonged parallel irradiation at 313 nm of degassed pentane solutions of the stilbenes and the *m,m'*-dibromostilbenes over mossy zinc give large amounts of dibromophenanthrene from the latter (50 per cent, identification based on g.l.p.c. retention time) and very little phenanthrene from the former (five per cent).

and the dependence on azulene would deviate somewhat from linearity, with $r_d > r_s^4$.

Using Förster's theory for long-range singlet energy transfer a value of $K_s = 15 M^{-1}$ can be calculated which is based on the spectral overlap between *trans*-stilbene fluorescence and azulene absorption^{1,4}. In the case of the bromostilbenes a smaller K_s value could result if τ_{1t} is decreased owing to enhanced intersystem crossing. Examination of the data in *Table 4* shows that $K_s \approx r_d$ (equation 20) for the cases of the stilbenes, the *m*-bromostilbenes and the *m,m'*-dibromostilbenes but that r_d approaches r_s in the case of the *p*-bromostilbenes. It follows that bromine enhances intersystem crossing when bonded at a para position, but is completely† ineffective in this respect when bonded at a meta position. This striking positional dependence of radiationless heavy-atom induced spin-orbital coupling is to our knowledge unprecedented. The relatively modest positional dependence observed in dibromonaphthonorbornenes is not analogous since substitution was not directly on a carbon of the π -system as in the bromostilbenes⁶³.

The *p*-bromostilbene data correspond to neither of the limiting cases described by equations 20 and 21 and require the use of equation 19 for their explanation. A fitting of the data to equation 19 can be accomplished by (1) using K_t and α from the benzophenone-sensitized experiments, (2) assuming $\Phi_{1c1p} = 1 - \Phi_{DHP} \approx 0.9$ as in the case of the unsubstituted stilbene⁵⁹, and (3) estimating the quantum yield of the non-activated process competing with fluorescence, presumably Φ_{is}^{1t} , from the temperature dependence^{52, 53} of *trans-p*-bromostilbene fluorescence^{1, 64}. The values of Φ_{is}^{1t} obtained from the fluorescence data suggest that approximately 30 per cent of *trans-p*-bromostilbene singlets intersystem cross at 30°. The functioning of this additional decay channel is expected to decrease the lifetime of *trans* singlets by about 30 per cent resulting in $K_s \approx 10 M^{-1}$ for *trans-p*-bromostilbene (~ 70 per cent of $14 M^{-1}$, see *Table 4*). The value of β can be calculated from $([t]/[c])_s$ at zero azulene concentration using the measured value of ϵ_s/ϵ_t at the excitation wavelength. An appropriate value of Φ_{is}^{1p} is finally chosen which fits equation 19 to the experimental photostationary states at all azulene concentrations. Observed and calculated photostationary compositions for the direct photoisomerization of the *p*-bromostilbenes in *n*-pentane employing 313 and 254 nm excitation conditions are shown in *Table 5*. It can be seen that excellent agreement with the experimental observations is obtained by using Φ_{is}^{1p} values of 0.28 and 0.48 for the 313 and 254 nm experiments, respectively. The assumption of the same Φ_{is}^{1t} value at the two wavelengths is probably justified since preliminary measurements indicate that Φ_f of *trans-p*-bromostilbene is also the same. The difference in the Φ_{is}^{1p} values may suggest that *Scheme 3* should include an additional intersystem crossing step which operates following 254 nm excitation. Speculation concerning such a step would be premature since the difference may not be significant when compared with the experimental uncertainty of the measurements.

Barring large substituent effects on the effective rate constant for triplet

† The value of $r_d = 23 M^{-1}$ for the *m,m'*-dibromostilbenes may indicate a tiny intersystem crossing component in this case, but may be within experimental uncertainty of $15 M^{-1}$. A value of $r_d = 12 M^{-1}$ was obtained for this compound in benzene. Cf., however, note added in proof.

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excitation transfer to azulene (see equation 17), the relative magnitude of the r_s values in Table 4 should be related approximately to the inverse of the rate constant for intersystem crossing from 3p . Examination of these values suggests a pronounced enhancement of k_d for bromine substitution at the para position and little or no enhancement when bromine is bonded at a meta position.

Table 5. The azulene effect on the direct photoisomerization of the *p*-bromostilbene in *n*-pentane at 30°

313 nm			254 nm		
[Az] × 10 ³ M	%[t] _{calc} †	%[t] _{obs}	[Az] × 10 ³ M	%[t] _{calc} ‡	%[t] _{obs}
0	11.0	11.0§	0	61.8	61.8§
5.0	12.4	12.4	7.6	67.9	67.8
9.0	13.5	13.7	15.1	72.3	73.1
12.5	14.5	14.4	22.7	75.8	76.0
20.0	16.5	16.5	30.3	78.6	78.5
25.0	17.8	18.0			

† From equation 19 using $\phi_{is}^{3p} = 0.28$, $\phi_{is}^{3s} = 0.31$, $\alpha = 0.396$, $\beta = 0.462$.

‡ From equation 19 using $\phi_{is}^{3p} = 0.48$, $\phi_{is}^{3s} = 0.31$, $\alpha = 0.396$, $\beta = 0.479$.

§ These values are those predicted by the intercepts of the azulene plots.

The positional dependence is probably related to the difference between meta and para coefficients of the highest occupied and lowest unoccupied MOs of stilbene, $c_m = 0.0791$ and $c_p = 0.3138$ in the Hückel approximation. Spin-orbit coupling occurs via interaction with upper $\sigma\pi^*$ and $\pi\sigma^*$ singlet and triplet states^{65,66}. Qualitatively, spin-orbit coupling matrix elements can be approximated by one centre term and can be reduced to a centre by centre sum of the π -electron coefficients times the approximate σ orbital coefficients⁶⁶. If, as in the case of bromine substitution the centre bearing bromine dominates then the expression describing the probability of spin-orbital coupling will be dominated by the appropriate π and σ MO coefficients at that centre.⁶⁶ It is sensible, therefore, that since the π -coefficient of stilbene is nearly zero at the meta position, substitution at that position should cause no enhancement in the rate constants for intersystem crossing.

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⁶⁶ B. R. Henry, personal communication.

NOTE ADDED IN PROOF

Recent observations by D. W. L. Chang and A. Marinari in our laboratory have led us to conclude that intersystem crossing yields based on photo-stationary states for the direct photoisomerization of the stilbenes in the presence of azulene are not reliable. Much larger azulene effects are observed on the initial $t \rightarrow c$ quantum yields for the direct photoisomerization. A preliminary analysis of these data together with the temperature dependence of the fluorescence yields of the *trans*-stilbenes in *n*-pentane gives the quantum yields shown in Table 6. While a positional dependence of the heavy

Table 6. Revised preliminary intersystem crossing yields

Compound	$\Phi_{\text{is}}^{\text{t}}$	$\Phi_{\text{is}}^{\text{p}}$
Stilbene	0.00	0.34
<i>p</i> -Bromostilbene	0.31	1.00
<i>m</i> -Bromostilbene	0.16	0.86
<i>m,m'</i> -Dibromostilbene	0.37	0.84

atom effect is still apparent it is much more modest than had been previously supposed.