CIS–TRANS ISOMERIZATION OF STYRENES VIA THE TRIPLET PATHWAY: THE PERPENDICULAR TRIPLET STATE OBSERVED BY LASER FLASH PHOTOLYSIS

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Summary

The kinetics of the *cis–trans* photoisomerization of 1-phenylcyclohexene via the triplet state, studied by either nanosecond pulse radiolysis or laser flash photolysis in the presence of sensitizers, reveal that the triplet species involved in the isomerization mechanism has a lifetime of 55 ns in fluid solution at room temperature. A transient absorption decaying with the same 55 ns lifetime, and therefore assigned to this triplet species, was observed in the 320 - 345 nm region. Quite similar triplet–triplet absorptions were observed with 1-phenylcycloheptene, 1-phenylpropene and styrene itself. From the experimental results and from considerations of the energy surfaces of the excited states of styrene, the observed triplet species is identified as the perpendicular (or "phantom") triplet state of the styrene moiety.

1. Introduction

Cis–trans photoisomerization of styrene, stilbene and similar molecules is known to be possible via two different mechanisms: a singlet and a triplet pathway. For stilbene and its derivatives the triplet pathway has been extensively studied using continuous irradiation [1, 2] but little is known about the triplet intermediates, especially the "phantom" perpendicular triplet. A triplet species, which has been observed by pulse radiolysis of stilbene [3] and flash photolysis of nitrostilbenes [4], gave indications of being non-planar but this species was not clearly identified as the perpendicular triplet. Reasons for this uncertain assignment will be discussed later.

Of course it is impossible to follow the *cis–trans* isomerization of styrene itself and even for 2-substituted styrenes detection using spectroscopy is nearly impossible since the absorption spectra of *cis-* and *trans-* 1-phenylpropene for example are very similar. However, with compounds

such as 1-phenylcyclohexene (PC6) and 1-phenylcycloheptene (PC7), which can be considered as 1,2-disubstituted styrenes, this difficulty does not arise. We have recently shown that the *trans* form of these molecules does exist as a transient species but with lifetimes that are several orders of magnitude larger than the time required for the *cis—trans* isomerization process to occur [5, 6]. The absorption spectrum of these highly strained *trans* species is strongly red shifted with respect to that of the stable *cis* starting product ($\lambda_{max} \approx 300$ and 380 nm for *trans* PC7 and *trans* PC6 respectively whereas $\lambda_{max} \approx 248$ nm for the *cis* form). Thus the kinetics of the appearance of the *trans* species after a short excitation pulse can be readily observed by fast spectroscopy techniques and give information on the lifetime of any intermediate involved in the *cis—trans* photoisomerization process.

2. Experimental

Commercially available 1-phenylcyclohexene (Aldrich Chemical) was checked by gas phase chromatography (GPC) and used without further purification. 1-Phenylcycloheptene was synthesized by a Grignard addition to the cycloheptanone (Aldrich Chemical) followed by dehydratation of the alcohol. GPC analysis of the 1-phenylcycloheptene obtained revealed the presence of 2% 1-phenylcyclohexene which at this low percentage was not considered to be a disturbing impurity.

Since the quantum yields of intersystem crossing are extremely low for the phenylcycloalkenes [7], direct photolytic excitation is quite inefficient for a study of the triplet pathway of isomerization. Thus, the triplet state was populated by flash photolysis using a sensitizer and by pulse radiolysis in benzene (which to a first approximation is a sensitization technique, the solvent being used as sensitizer). In both cases the concentration of phenylcycloalkene has to be fairly high in order to obtain a nearly total energy transfer in a few nanoseconds. Assuming for the triplet—triplet energy transfer a rate constant of around 6×10^9 M^{-1} s^{-1}, it can be calculated that a 95% energy transfer will be obtained after 5 ns with an acceptor concentration of 10^{-1} M if the triplet lifetime of the sensitizer is in the microsecond range or larger. But in pulse radiolysis experiments where the triplet benzene, which is the energy donor, has a very short lifetime (about 3 ns in liquid benzene [8]) even higher concentrations of phenylcycloalkenes (typically ranging from 2×10^{-1} up to 5×10^{-1} M) have to be used in order to get a high energy transfer yield.

In laser photolysis experiments the sensitizer has to be carefully chosen. It must possess the following properties: (a) a triplet energy larger than 62 kcal mol^{-1}; (b) a non-negligible extinction coefficient at 353 nm (third harmonic of the neodymium laser; excitation at 265 nm is impossible since the absorbance of a 10^{-1} M solution of phenylcycloalkenes is several hundred optical density units per centimeter at 265 nm); (c) an absorption spectrum falling sharply either for wavelengths longer than 353 nm (to permit

the observation of transient absorptions in the 370 - 420 nm range where the absorption band characteristic for the *trans* phenylcyclohexene appears) or for wavelengths shorter than 353 nm (to permit absorption measurements in the region 290 - 350 nm). We used xanthone in the first case and thioxanthone in the second; both were in benzene solution in order to minimize complications arising from hydrogen abstraction from the solvent, a typical reaction for the benzophenone-like sensitizers.

For the pulse radiolysis experiments we used the apparatus of the Christie Hospital and Holt Radium Institute in Manchester (Gt. Britain). This LINAC source provides 10 ns pulses with doses around 6 krad; the coupled analytical system has a response time of about 5 ns.

For laser flash photolysis experiments the excitation pulses were provided by the third harmonic (353 nm) of a passively Q-switched Nd^{3+} laser (Quantel) equipped with a pulse slicer giving 3 ns pulses and three amplifiers. The response time of the spectroscopic analytical system was less than 3 ns in this case.

3. Results

3.1. Pulse radiolysis measurements

Typical oscilloscope traces obtained at 390 nm by pulse radiolysis of phenylcyclohexene (PC6) and phenylcycloheptene (PC7) at a concentration of 5×10^{-1} M in benzene are shown in Fig. 1.

The transient absorption observed with the PC7 solutions is mainly due to the radical anion of the solute. The absorption spectrum measured at the end of the excitation pulse (Fig. 2) is quite similar to that previously reported for the styrene radical anion [9] and the absorption decays according to a complex kinetics which fits roughly (Fig. 3) the relation $DO_t = A + Bt^{-1/2}$, a classical relation for the decay of radical ions [10].
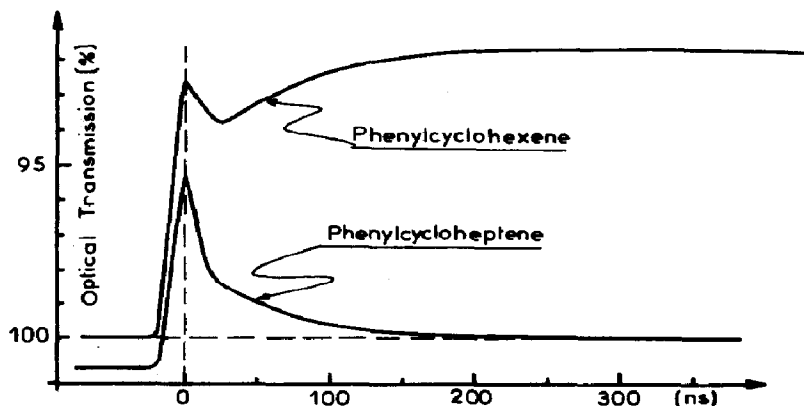

Fig. 1. Transmission changes at 390 nm after the excitation of benzenic solutions of phenylcyclohexene and phenylcycloheptene (5×10^{-1} M) by a 6 krad, 20 ns electron pulse.
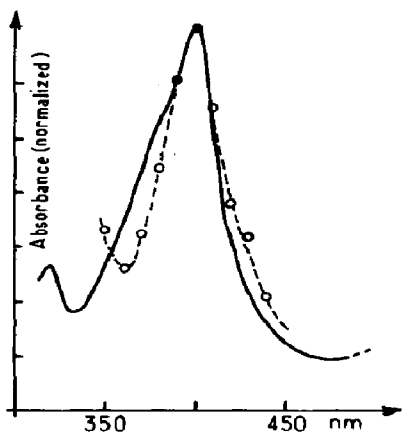
Fig. 2. Absorption spectra of the styrene radical anion (——) after ref. 9 and the transient species (O—O) produced by pulse radiolysis of phenylcycloheptene in benzene (spectrum measured at the end of the excitation pulse).
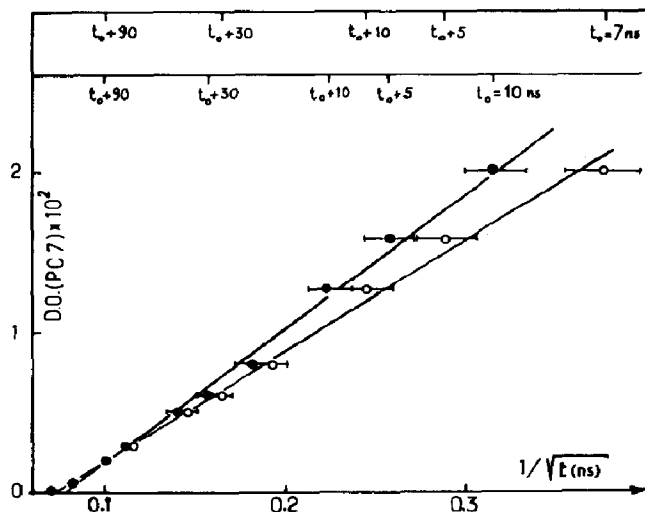

Fig. 3. Kinetic analysis of the decay of the transient absorption at 390 nm observed in pulse radiolysis of phenylcycloheptene in benzene. As the excitation pulse duration is 20 ns the time origin is rather inaccurate. Two plots are drawn with t_0 (maximum absorption) equal to 7 ns (O) and 10 ns (●).

For the PC6 solutions the transient absorption observed in the range 360 - 430 nm is clearly due to two transient species. (a) The first species which grows during the excitation pulse and then decays very rapidly is responsible for the small maximum during the first 20 ns. It is certainly the same type of species as the one observed with phenylcycloheptene. Its absorbance as a function of wavelength, with a maximum at 400 nm, follows closely the absorption spectrum presented in Fig. 2. It is thus assigned to the PC6 radical anion. (b) The second species which grows for 200 ns and more is identified as *trans*-PC6 since it decays with a first order rate constant of

1.1×10^5 s^{-1}. Its absorption is maximal in the 370 - 390 nm range and it is not observed with PC7, the *trans* form of which absorbs around 300 nm.

Since on the one hand the triplet lifetime of the donor benzene is short and the energy transfer so fast that the PC6 triplet is populated in a few nanoseconds and since on the other hand the formation of *trans*-PC6 by direct excitation (in laser photolysis at 265 nm) is also very rapid (less than 5 ns), the slow growth of the *trans* form in pulse radiolysis experiments clearly demonstrates that a triplet precursor of *trans*-PC6 has a lifetime of about 50 ns.

To get a more precise value of this precursor lifetime, the transient absorption DO_1 due to the radical anion must be subtracted from the total transient absorption DO_{PC6} and the resulting difference ΔDO which gives the absorption of the *trans* species can then be analyzed as

$$\Delta DO = DO_0 + (DO_{max} - DO_0)[1 - \exp\{-k(t - t_0)\}]$$

where DO_0 is the absorption of the *trans* species produced at time t_0 (end of the excitation pulse) via both singlet and triplet pathways, DO_{max} is the maximum absorption of the *trans* species measured 300 ns after the excitation and k is the reciprocal lifetime of the precursor. It is further assumed that: (1) The decay of the *trans* species during the considered range of time (about 200 ns) is negligible since the *trans*-PC6 lifetime is around 10 μs; (2) the annihilation of the radical anions does not give rise to an appreciable amount of excited states (and therefore to *trans* species) in comparison with the quantities produced during the excitation pulse. The second assumption seems to be justified since in benzene the yield of the radical species is small compared with the yield of excited states. In addition, we may assume that the kinetic behaviour of the radical anions is identical for PC6 and PC7 so that $DO_1 = f(t)$ is given by the transient absorption DO_{PC7} observed with phenylcycloheptene. Thus

$$\Delta DO = DO_{PC6} - DO_{PC7}$$

and

$$\ln(DO_{max} - DO_{PC6} + DO_{PC7}) = \ln(DO_{max} - DO_0) - k(t - t_0)$$

This relation is plotted in Fig. 4, together with the relation

$$\ln(DO_{max} - DO_{PC6}) = \ln(DO_{max} - DO_0) - k(t - t_0)$$

obtained when no correction is made for the absorption of the radical anion. The correction greatly improves the linearity of the plot during the first 50 ns but the lifetimes obtained from the linear parts of the two plots are not greatly different. It is found that $1/k = 56$ ns with the correction and 60 ns without the correction.

No transient absorption decaying with a 55 ns lifetime and thus assignable to the triplet precursor was found in the wavelength region 370 - 500 nm.
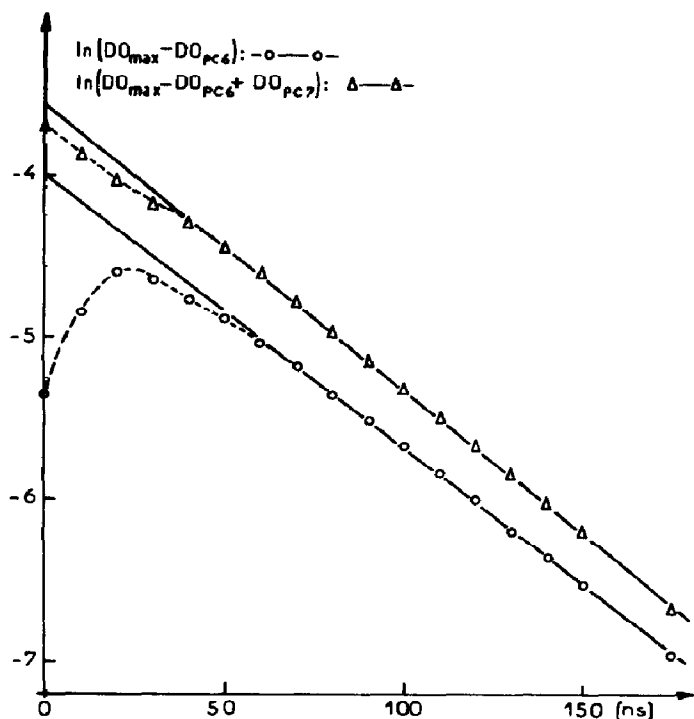
Fig. 4. Kinetic analysis of the growth of the *trans* phenylcyclohexene absorption at 390 nm: △——△, corrected for the absorption of the radical anion species; ○——○, uncorrected.

3.2. Laser photolysis measurements

Benzene solutions containing xanthone or thioxanthone[†] and 10^{-1} M phenylcyclohexene were excited by 3 ns laser pulses at 353 nm. Prior to excitation N_2 was bubbled through the cell for a few minutes to remove most of the dissolved oxygen.

The transient absorption, which is characteristic of *trans*-PC6, is observed in the 360 - 430 nm range with xanthone and in the 395 - 430 nm range with thioxanthone. This absorption grows for about 250 ns (Fig. 5(a)). It was checked that this slow growth is not related to a slow rate of energy transfer from the triplet sensitizer to the PC6. Indeed, the growth kinetics of the absorption are not affected by a change of the PC6 concentration from 5×10^{-2} to 2×10^{-1} M. Furthermore, the measured rate of energy transfer was found to be 5×10^{9} M^{-1} s^{-1} by following the decrease of the lifetime of the thioxanthone triplet at 550 nm as a function of the acceptor concentra-

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[†]The sensitizer concentration was adjusted so that 50% of the laser light was absorbed in the volume (0.2 cm depth, 1.0 cm length) through which the analytical beam passed (crossed beams arrangement).
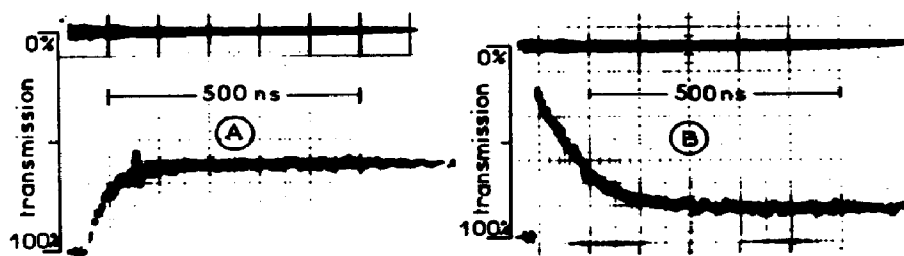
Fig. 5. Oscilloscope traces obtained by laser flash photolysis of a benzenic solution containing thioxanthone as sensitizer and 10^{-1} M phenylcyclohexene as acceptor: (a) λ = 395 nm, growth of the *trans* phenylcyclohexene absorption; (b) λ = 330 nm, decay of the absorption of the perpendicular triplet, precursor of the *trans* species.

tion in the range 1×10^{-3} - 5×10^{-3} M. Therefore with a PC6 concentration of 10^{-1} M the energy transfer is nearly complete after less than 10 ns.

The kinetics analysis of the growth of *trans*-PC6, according to the relation $\ln(DO_{max} - DO_t) = \ln(DO_{max}) - kt$, gives for the precursor of the *trans* species a lifetime $\tau = 1/k = 55 \pm 3$ ns, a value identical to that obtained from pulse radiolysis measurements.

When PC7 was used as the acceptor no transient absorption was detectable in the range 380 - 420 nm; this confirms that the transient absorption observed in pulse radiolysis of this compound was related to radical species and not to the PC7 triplet.

In the 320 - 345 nm region, using thioxanthone as sensitizer, a strong absorption was observed with either PC6 or PC7 as acceptor (Fig. 5(b)). This absorption grows within 10 ns and then decays in two steps: an initial fast decay lasting 200 - 300 ns followed by a slow decay lasting several microseconds. The slow decay is clearly related to the absorption of the *trans* species as shown by its lifetime and its wavelength dependence. The absorption spectrum measured after 500 ns increases in going from 320 to 345 nm for PC6, the *trans* form of which has a maximum absorption at 380 nm [5]. In contrast, for PC7, the *trans* form of which has a maximum absorption around 300 nm [6], there is an increase in going from 345 to 320 nm. As the kinetic behaviour of the *trans* species (growth and decay) is known, its contribution can be subtracted from the total transient absorption observed in the 320 - 345 nm region. The remaining short-lived transient absorption is then found to decay according to first order kinetics with a lifetime of 60 ± 3 ns. This lifetime, which is nearly identical to that obtained from the analysis of the growth of *trans*-PC6, strongly suggests that the short-lived transient absorption must be assigned to the triplet precursor of the *trans* species. This is further corroborated by the fact that in aerated solutions both the growth of the *trans* species and the decay of the short-lived transient are modified in the same proportion. The corresponding lifetimes are both around 34 - 35 ns in aerated solutions.

Since the oxygen concentration in aerated benzene is around 1.9×10^{-3} M [11] a rate constant for quenching by O_2 of the triplet precursor of

the *trans* species was calculated from the lifetimes in nitrogen-saturated and aerated solutions to be 6.4×10^9 M^{-1} s^{-1}.

A similar short-lived (40 - 50 ns) transient absorption is observed in the same 320 - 345 nm region when 1-phenylpropene or styrene itself are used as acceptors instead of phenylcycloalkenes. A study of the properties of these non-cyclic styrenes is under investigation but these first results with styrene clearly demonstrate that the short-lived transient cannot be an unstable conformer of the *trans* ground state of the phenylcycloalkenes similar to the one proposed [12] for acetylcyclohexene (see also ref. 13).

4. Discussion

It is clear that the precursor of the *trans* species is a triplet state. On account of the high concentrations of substrates used in the experiments reported earlier, the possible role of a triplet excimer was examined and can be discarded. Indeed, if the binding energy is much lower for a triplet excimer than for a singlet excimer (as is generally accepted) it can be calculated that with concentrations of substrates around 10^{-1} M, the relative amount of triplet excimer should be a few percent or less so that a triplet excimer would not substantially change the kinetic properties of the triplet state. Furthermore, this percentage of triplet excimer should be a nearly linear function of the ground state concentration. That is to say, if the transient absorption at 330 nm were due to a triplet excimer, its intensity should increase by a factor of four when the substrate concentration is changed from 5×10^{-2} M to 2×10^{-1} M; this is contrary to observation.

Our contention is that the triplet state observed is relaxed by a 90° twist of the double bond. Indeed the energies of triplet xanthone ($E_T \approx$ 74 kcal mol^{-1}) and thioxanthone ($E_T \approx 65.5$ kcal mol^{-1}) [11] are certainly transferred to the lowest triplet state of the styrene moiety of the acceptor which, in the planar conformation, lies around 61 kcal mol^{-1} above the ground state [14, 15]. This triplet, T_1, was shown to be correlated to the second excited singlet state S_2 [15] an "ethylenic" state, whereas a "benzenic" triplet state T_2 probably corresponds to the benzenic S_1 state*. This second triplet T_2 probably lies at about 72 kcal mol^{-1} above the ground state if it is assumed that the singlet–triplet splitting is nearly the same for benzene and for benzenic states of styrene. Thus there is no crossing of the benzenic and ethylenic triplet surfaces in contrast to what happens for the two first excited singlet states. Here an avoided crossing creates an energy minimum for the untwisted S_1, which explains how

*The notation of benzenic and ethylenic states in styrene is derived from theoretical calculations [16] which indicate that for the non-twisted styrene the excitation is mainly localized on the benzene π system in S_1 (benzenic) and on the double bond π system in S_2 and T_1 (ethylene). These calculations also show that there is no stabilization of the non-twisted triplet T_1.

fluorescence can compete with cis–trans isomerization [16]. Therefore, the energy surface of the lowest triplet state of styrene, like that of a simple olefin, is expected to exhibit a single energy minimum for a 90° twist of the double bond. The untwisted conformation of this triplet is an unstable geometry, corresponding to a maximum energy, and therefore has a negligible lifetime. This agrees with the fact that phosphorescence of styrene-like molecules has never been observed [17] and this implies that the metastable triplet species observed must be the perpendicular conformation.

The situation is completely different for the stilbene system (Fig. 6). In this case the trans triplet can be stabilized in an energy well resulting from an avoided crossing between the two lowest triplet surfaces [18]. There are thus at least two stable conformations for the triplet: trans and perpendicular (the problem of the stability of a cis triplet being further complicated by steric hindrance). This raises difficulties for a precise assignment of the transient triplet species observed in laser flash photolysis of nitrostilbenes [4]. The efficient quenching of this species by azulene and ferrocene and the decrease of the photoisomerization quantum yield Φ_{t-c}, in the presence of ferrocene [19] or azulene [2] seem to rule out an identification of the perpendicular triplet: the energy gap between the perpendicular triplet and ground states is much too small for an energy transfer to these quenchers and the quenching of the perpendicular triplet should not affect Φ_{t-c}. In contrast, the fact that the same transient is observed by excitation of both cis and trans nitrostilbenes and also that the quenching of the transient by
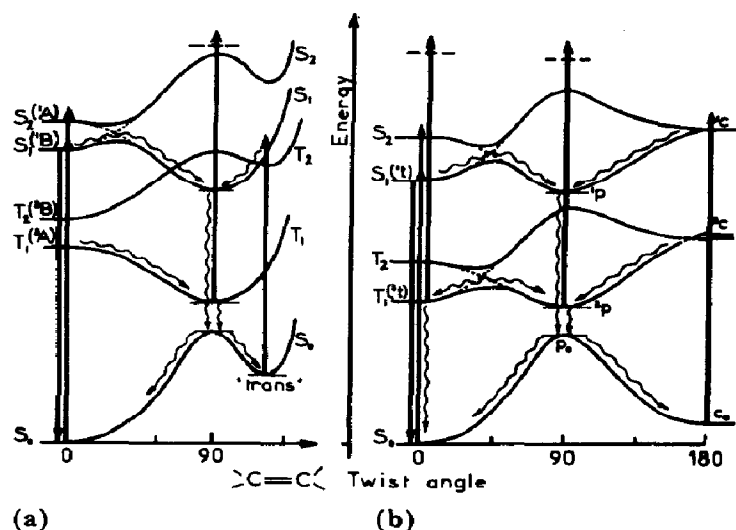

Fig. 6. Possible energy surfaces for the S_0, T_1, S_1, T_2 and S_2 states of (a) a phenylcycloalkene (e.g. 1-phenylcycloheptene) and (b) stilbene. Double arrows indicate absorption or emission processes and wavy arrows show some of the most important non-radiative processes. The figure illustrates the similarities and the differences expected for the photophysical behaviour of these two types of molecules. The two possible triplet–triplet absorptions of stilbene are drawn.

O_2 does not change Φ_{t-c} seems to indicate that the observed species could be the perpendicular triplet [4, 19].

The above results may be rationalized only by assuming one of the following processes: a very fast equilibration between the *trans* and perpendicular triplets† (but it is then impossible to assign the observed transient to one of these two triplet conformations); and/or a special type of quenching of the perpendicular triplet by azulene (and probably ferrocene) according to the scheme

$$^3p + Az \ \rightleftarrows \ ^3[p{-}Az] \ \rightleftarrows \ ^3[t{-}Az] \ \rightarrow \ trans + {}^3Az$$
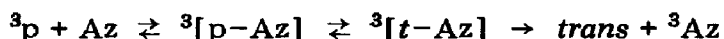
proposed by Saltiel [2] to account for the dependence of the rate constant for quenching by azulene on temperature and solvent viscosity.

From very recent results [20] it seems that the absorption spectra of the *trans* and perpendicular triplet states may be distinguished: the *trans* triplet shows a rather sharp band at 380 nm and a less intense broad band at 360 nm similar to the absorption spectrum obtained ten years ago [21, 22] in a rigid medium at 77 K, whereas the perpendicular triplet state shows only one broad band absorption with a maximum at around 350 - 360 nm.

Acknowledgments

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† Evidence for the existence of this equilibrium is announced in ref. 19 as "to be published".

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