# OBSERVATION OF A TRIPLET STATE OF AZULENE GENERATED BY ENERGY TRANSFER IN SOLUTION

H. GÖRNER and D. SCHULTE-FROHLINDE

*Institut für Strahlenchemie, Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d. Ruhr (F.R.G.)*

## Summary

Absorption of a transient was observed by laser flash photolysis in the 340 - 400 nm range ($\lambda_{max}$ = 360 nm) after energy transfer from various triplet donors to azulene. The transient lifetime at room temperature (3 - 5 $\mu$s) is essentially independent of solvent properties and of the nature of the triplet donor. Rate constants for quenching the transient by oxygen are higher than those for aromatic triplets. Quenching of aromatic triplets by azulene in various solvents is almost diffusion controlled provided that the triplet energy of the donor is greater than 200 kJ mol$^{-1}$. Assignment of the transient to a triplet state of azulene is therefore suggested. Ferrocene gave very similar rate constants for triplet quenching but no transient absorption.

## 1. Introduction

Energy transfer from high energy triplet donors to azulene is a well-known process [1 - 5]. Saltiel *et al.* [5] have recently shown that energy transfer from the triplet state of indeno[2,1-a]indene to azulene is a fully diffusion-controlled process. Energy transfer from arylethylenes to azulene has proved to be a successful method for studying the mechanism of *cis—trans* photoisomerization of stilbenes [6 - 8] and related compounds [9, 10]. Using flash photolysis techniques, Herkstroeter [4] has determined the triplet energy $E_T$ of azulene to be approximately 163 kJ mol$^{-1}$ by triplet quenching. This value is supported by values from theoretical calculations, which range from 142 to 172 kJ mol$^{-1}$ [11], but is in conflict with an estimated 0–0 phosphorescence band at 126 kJ mol$^{-1}$, reported by Rentzepis [12]. However, absorption of an azulene triplet species seems not to have been reported in the literature so far (compare refs. 1, 4, 13, 14). We now present evidence for triplet–triplet absorption of azulene under sensitized excitation conditions. In addition, rate constants for quenching of the azulene triplet by oxygen and of several aromatic triplets by azulene, ferrocene and oxygen are presented.

## 2. Results and discussion

The experiments were carried out by nanosecond laser photolysis using mainly the third harmonic of a neodymium laser ($\lambda_{exc}$ = 353 nm; pulse width, 10 ns; energy $\leqslant$ 50 mJ) and an appropriate detection system (transient digitizer R 7912), as described elsewhere [7, 8]. On excitation of triplet donors in the presence of azulene (Aldrich) a transient appeared within the rise time of the laser pulse (approximately 10 ns) in the 360 - 420 nm region. This transient was not observed in the absence of either the triplet donor or azulene. As a representative example, the absorption spectrum of the observed transient is shown in Fig. 1 for benzene solutions containing benzo- phenone and azulene. On excitation at 353 nm it was not possible, except with benzophenone, to measure a transient absorbance ($\Delta A$) at wavelengths shorter than 360 nm owing to substantial ground state absorption of azulene (typically $10^{-3}$ M) and the donors (typically $10^{-2}$ M). In order to measure the transient absorption maximum in other cases, the fourth harmonic of the neodymium laser ($\lambda_{exc}$ = 265 nm) and concentrations of azulene and donors of approximately $10^{-4}$ M were used. For acetonitrile solutions of azulene containing either benzophenone (Fig. 1), biphenyl or triphenylene as triplet donors, absorption maxima at 360 nm were observed for the transient, hereafter called the 360 nm transient. Using $7.6 \times 10^3$ $M^{-1}$ $cm^{-1}$ for the molar extinction coefficient of the benzophenone triplet [15] and assuming the absence of energy wastage, a molar extinction coefficient of
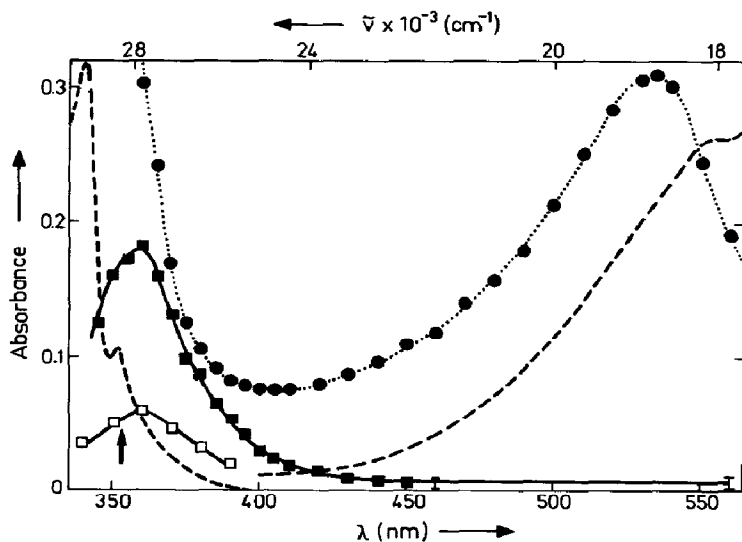


Fig. 1. Transient absorption spectrum of deoxygenated solutions at 25 °C containing benzophenone and azulene at 10 ns (··●··) and 500 ns (–□–, –■–) after the laser pulse: □, acetonitrile, $\lambda_{exc}$ = 265 nm, [benzophenone] = $1 \times 10^{-4}$ M, [Az] = $2 \times 10^{-4}$ M (where Az denotes azulene); ●, ■, benzene, $\lambda_{exc}$ = 353 nm (indicated by the arrow), [benzophe- none] = $1 \times 10^{-2}$ M, [Az] = $1 \times 10^{-3}$ M; –––, relative ground state absorption (magnifica- tion at $\lambda$ > 400 nm, 20×).

$4 \times 10^3$ M$^{-1}$ cm$^{-1}$ was derived from Fig. 1 for the 360 nm transient in benzene.

Decay kinetics of the 360 nm transient were measured between 370 and 400 nm using $\lambda_{exc}$ = 353 nm throughout. At low laser intensities the transient decay was first order and the effective lifetime ($\tau^{360} = k_{obsd}^{-1}$) was found to be independent of the concentration [Az] of azulene in the range $4 \times 10^{-4}$ - $4 \times 10^{-3}$ M (Fig. 2). At high laser intensities the contribution of a second-order transient decay was observed. The 360 nm transient showed no significant differences in its spectra and kinetic behaviour for the eight different triplet donors used (Table 1). The lifetime of the 360 nm transient in several solvents ranged from 3 to 5 $\mu s$ and was practically independent of temperature between 25 and 70 °C (Table 1).

The transient lifetime was efficiently reduced by the addition of oxygen. In air-saturated benzene solutions lifetimes of 60 - 100 ns and the same yields (as measured from the $\Delta A$ value immediately after the laser pulse) as in degassed solutions were found for the 360 nm transient. However, in oxygen-saturated solutions the 360 nm transient could not be observed. This was due to the expected short lifetime of the transient (less than 20 ns) and the concomitant occurrence of fluorescence during the laser pulse. The fluorescence originates from the $S_2$ state of azulene which was populated by direct light absorption at 353 nm (see refs. 13, 14, 19 - 23). From transient
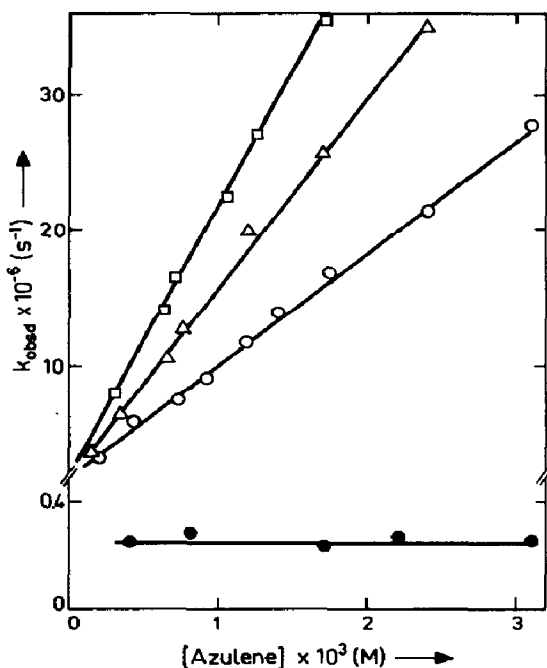


Fig. 2. First-order decay rate constant of the 360 nm transient in benzene (●) and of the benzophenone triplet at 535 nm (□, △, ○) as functions of the azulene concentration in deoxygenated solutions of $n$-pentane (□), acetonitrile (△) and benzene (○) at 25 °C: $\lambda_{exc}$ = 353 nm; [benzophenone] = $1 \times 10^{-2}$ M.

TABLE 1

The lifetime of the 360 nm transient and rate constants for quenching by oxygen

| Sensitizer | Solvent | $\tau^{360a}$ ($\mu s$) | $k_{ox}^{360} \times 10^{-9}$ ($M^{-1}$ $s^{-1}$) | $k_{ox}^{sens} \times 10^{-9\,b}$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|
| Xanthone | Benzene | $4^c$ $(3)^d$ | 6 | $5.6^e$ |
| Benzophenone | | $4^c$ (3) | 6 | $3.0^e$ |
| 9-Bromophenanthrene | | 3 | | 2.2 |
| 2-Acetonaphthone | | $3^c$ (2.5) | 7 | $1.9^e$ |
| 2-Nitronaphthalene | | $3^c$ (3) | 7 | 2.2 |
| Chrysene | | 3 | | $1.0^f$ |
| Anthracene | | 3 | | $3.1^e$ |
| | | | | $2.9^f$ |
| 9-Bromoanthracene | | 4 | 6 | 3.3 |
| Benzophenone | n-Pentane | 3 | 7 | 1.8 |
| | Acetonitrile | 3 (3) | 8 | 3.4 |
| | Toluene | 4 (3) | 7 | 3.0 |
| | tert-Butyl alcohol | 3 (3) | 7 | 2.7 |
| 2-Nitronaphthalene | n-Pentane | 4 | 5 | 1.0 |
| | Acetonitrile | 2, $4^c$ | 8 | 1.5 |
| | Methanol | 2, $5^c$ | | 1.5 |
| | Toluene | 2, $4^c$ | 6 | 1.2 |
| | tert-Butyl alcohol | 3, $5^c$ | 5 | 1.4 |

At 25 °C (26 °C for tert-butyl alcohol).

[a] Unless indicated otherwise, samples were deoxygenated by purging with argon; values are lower limits for transient lifetimes owing to small amounts of oxygen and impurities which may be present.

[b] Oxygen concentrations in air-saturated solutions were $1.68 \times 10^{-3}$ M, $1.81 \times 10^{-3}$ M, $2.12 \times 10^{-3}$ M, $1.62 \times 10^{-3}$ M and $1.7 \times 10^{-3}$ M for acetonitrile, toluene, methanol, benzene and tert-butyl alcohol respectively (taken from ref. 16), and a value of $2.3 \times 10^{-3}$ M was assumed for n-pentane; the experimental error is ±10% and ±20% for $k_{ox}^{sens}$ and $k_{ox}^{360}$ respectively.

[c] Samples were deoxygenated by three freeze-pump-thaw cycles (at $1 \times 10^{-5}$ Torr); the experimental error in transient lifetimes is ±2 $\mu s$.

[d] Values in parentheses refer to measurements at 70 °C.

[e] Data taken from ref. 17.

[f] In cyclohexane; data taken from ref. 18.

lifetimes in the absence of air and in the presence of air, quenching rate constants ($k_{ox}^{360}$) were estimated (Table 1). Values for $k_{ox}^{360}$ in the range $(5 - 8) \times 10^9$ $M^{-1}$ $s^{-1}$ indicate a very efficient quenching process. For comparison, quenching rate constants ($k_{ox}^{sens}$) of the sensitizer triplets by oxygen (in the absence of azulene), using the triplet lifetimes in argon-, air- and oxygen-saturated solutions, are listed in Table 1 in addition to values from the literature [17, 18, 24]. Values for $k_{ox}^{360}$ are from two to five times larger than those for $k_{ox}^{sens}$.

The decay kinetics of the triplet donors in the presence of azulene were first order and the rate constant ($k_{obsd}^{sens}$) exhibited a linear dependence on [Az] as shown in Fig. 2 for typical examples. (No attempt was made to

evaluate the first- and second-order kinetics of the triplet donors in the absence of azulene; compare ref. 25.)

$$k_{\mathrm{obsd}}{}^{\mathrm{sens}} = \tau_{\mathrm{sens}}{}^{-1} + k_{\mathrm{az}}[\mathrm{Az}]$$

Quenching rate constants $(k_{\mathrm{az}})$ of 13 triplet donors, measured at the maximum $(\lambda_{\mathrm{obsd}})$ of the triplet–triplet absorption spectrum at 25 °C in benzene and several other solvents, are given in Table 2 and Table 3 respectively. For $E_{\mathrm{T}} \geqslant 190$ kJ mol$^{-1}$, values for $k_{\mathrm{az}}$ are almost unaffected by the nature of the donor but depend significantly on solvent viscosity $\eta$. A plot of $k_{\mathrm{az}}$ versus $\eta^{-1}$ for several solvents is shown in Fig. 3 for benzophenone and 2-nitro-naphthalene as sensitizers. According to the Debye equation a linear dependence is expected in the simplest case for $k_{\mathrm{az}}$ versus $\eta^{-1}$. Except for tert-butyl alcohol $k_{\mathrm{az}}$ is slightly less than the predicted value. This discrepancy may result from back reaction of the [sensitizer ... azulene] complex into separate molecules [5]. When azulene was replaced by ferrocene, $E_{\mathrm{T}} \approx 165$ kJ mol$^{-1}$ [4], essentially similar quenching rate constants $k_{\mathrm{fe}}$ were found in all cases examined (see Tables 2 and 3 and Fig. 3), in agreement with results from other groups of researchers [26 - 30]. We have carefully checked that

TABLE 2

Quenching rate constants of aromatic triplets by azulene and ferrocene in benzene solutions at 25 °C

| Number | Compound | $E_{\mathrm{T}}$ (kJ mol$^{-1}$) | $\lambda_{\mathrm{obsd}}$ (nm) | $k_{\mathrm{az}} \times 10^{-9}$ (M$^{-1}$ s$^{-1}$) | $k_{\mathrm{fe}} \times 10^{-9}$ (M$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|
| 1 | Xanthone | 310 | 610 | 8.5 | 10 |
| 2 | Benzophenone | 287 | 535 | 8 | 9 |
| | | | | | 8.6[a] |
| 3 | Triphenylene | 279 | 415 | 7 | 5.9[b] |
| 4 | Phenanthrene | 259 | 490 | 6.6 | |
| 5 | 9-Bromophenanthrene | 255 | 480 | 8.7 | |
| 6 | 2-Acetonaphthone | 248 | 430 | 8 | 5.4[b] |
| 7 | 2-Nitronaphthalene | 238 | 500 | 7 | 8.5 |
| 8 | Chrysene | 237 | 560 | 8 | 7 |
| | | | | | 5.7[a] |
| 9 | Fluorenone | 223 | 440 | 8 | 5.1[b] |
| 10 | Indeno[2,1-a]indene | 199 | | 8.6[c] | |
| 11 | Anthracene | 178 | 420 | 5 | |
| | | | | 7.4[d] | 4.4[a,b] |
| 12 | 9-Bromoanthracene | 172 | 430 | 4.5 | |
| 13 | 3,4:9,10-Dibenzopyrene | 168 | | 2.3[d] | 3.0[d] |

Samples were deoxygenated by purging with argon; $\lambda_{\mathrm{exc}} = 353$ nm. The experimental error in $k_{\mathrm{az}}$ and $k_{\mathrm{fe}}$ is ±10% and sensitizers 1 - 8, 11 and 12 are the same as in ref. 8.
[a] Data taken from ref. 26.
[b] Data taken from ref. 27.
[c] Estimated from ref. 5 taking into account the viscosity change for benzene and toluene.
[d] At 22 °C; data taken from ref. 4.

TABLE 3

Quenching rate constant $k_{az}$ of triplet states of aromatic compounds by azulene (ferrocene)

| Number | Compound | n-Pentane [0.23][a] | Aceto-nitrile [0.35] | Methanol [0.54] | Toluene [0.55] | Ethanol [1.1] | tert-Butyl alcohol[b] [3.6] |
|---|---|---|---|---|---|---|---|
| 1 | Xanthone | | 16 | 13 | | | 3.5 |
| 2 | Benzophenone | 20(21) | 14(18) | 11 | 7(9) | | 4.3 |
| 3 | Triphenylene | | | | 9 | (6.5)[c] | |
| 4 | Phenanthrene | 17 | 10 | 8.7 | | | 3.5 |
| 5 | 9-Bromophenanthrene | 18.5 | 13 | | | | |
| 6 | 2-Acetonaphthone | 21 | 14 | | 8 | (6.0)[c] | |
| 7 | 2-Nitronaphthalene | 26 | 14.5 | 9 | 10 | | 4.5 |
| 8 | Chrysene | 20 | 13 | 10.5 | 9.5 | | |
| 9 | Fluorenone | 24 | | | 7.5 | | |
| 10 | Indeno[2,1-a]indene[d] | 28.3 | 15.5 | | 9.6 | | 5.6 |
| 11 | Anthracene | 13[e] | | | 6.5 | (3.5)[c] | |
| 12 | 9-Bromoanthracene | 10 | 8 | | 5 | | |

Values are in units of $M^{-1}$ $s^{-1} \times 10^9$, the experimental error is ±10% and values in parentheses refer to ferrocene as the quencher. Unless indicated otherwise measurements were made at $\lambda_{exc}$ = 353 nm, 25 °C and samples were deoxygenated by purging with argon.

[a] Values in square brackets refer to viscosities in centipoise at 25 °C (cf. refs. 5 and 16).
[b] Measurements in tert-butyl alcohol were carried out at 26 °C throughout.
[c] Data taken from ref. 28.
[d] Extrapolated from data taken from ref. 5.
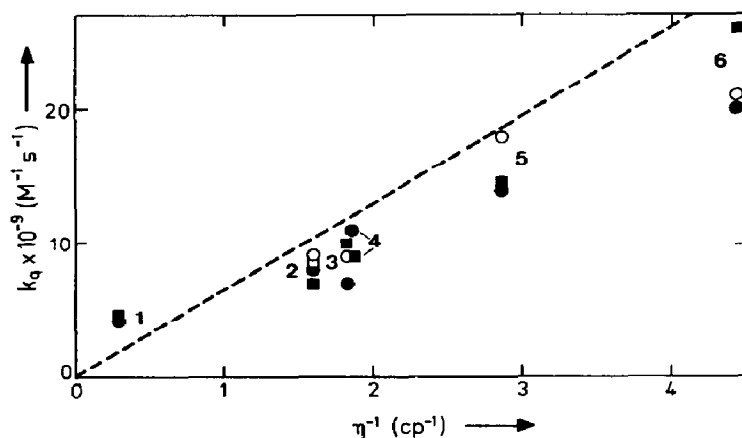[e] In hexane; data taken from ref. 1.



Fig. 3. Quenching rate constants $k_q$ of the triplet sensitizers by azulene (●, ■) and ferrocene (○, □) at 25 °C vs. $\eta^{-1}$ using benzophenone ($1 \times 10^{-2}$ M) (○, ●) and 2-nitronaphthalene ($1 \times 10^{-2}$ M) (□, ■) in tert-butyl alcohol (1), benzene (2), toluene (3), methanol (4), acetonitrile (5) and n-pentane (6): – – –, Debye equation $k_q = 8RT/3000\eta$ [5].

ferrocene exhibited no transient absorption ($\Delta A < 0.005$) in the 360 - 400 nm range when we used sensitizers 1, 2, 6 and 7 (Table 2). The absence of any ferrocene transient is in accordance with previous reports [4, 26].

With guaiazulene (1,4-dimethyl-7-isopropylazulene, EGA) and 4,6,8-trimethylazulene (Fluka) essentially the same results were obtained as with azulene. For example, a transient absorption in the 380 - 420 nm region (generated by transfer of triplet energy), a lifetime of 3 $\mu$s and $k_{az} = 7 \times 10^9$ $M^{-1}$ $s^{-1}$ were observed in benzene solutions containing benzophenone and guaiazulene. With 1,2-benzazulene (supplied by Rütgerswerke) in benzene, however, a transient ($\lambda_{max} = 430$ nm) was observable even on direct excitation.

Assignment of the 360 nm transient to the triplet state $^3Az^*$ of azulene is based on the following.

(1) Identical lifetimes of the 360 nm transient were observed (within experimental error) using different triplet donors, even those which do not carry a keto group (Table 1). This excludes the possibility that the 360 nm transient is a 1,4-biradical produced by an attack of the excited keto group on one of the double bonds of azulene. Furthermore, the 360 nm transient may not be assigned to an exciplex since in that case the transient lifetime would most probably be influenced by the nature of the triplet donor.
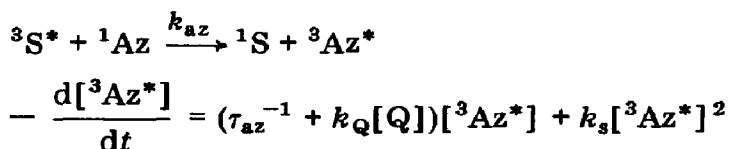
(2) Oxygen quenches the 360 nm transient with rate constants that are higher than those for high energy triplet states of aromatic compounds (Table 1). This effect is expected for triplet donors with lower triplet energies since Franck—Condon factors are larger than those for high energy triplet donors, owing to the smaller amount of energy that has to be converted into vibrational excitation. Considerably higher $k_{ox}$ values have also been observed in other cases of quenching of low energy triplets by oxygen [17, 18, 24, 31].

(3) The solvent polarity has only a small influence on the lifetime of the 360 nm transient (Table 1). This result is in accordance with the properties of other aromatic triplet states [16, 25]. Since the 360 nm transient is also observed in benzene, a solvent in which charge separation is not favoured, it is unlikely to be a radical anion or a radical cation.

(4) The observed first-order decay rate constant at low intensities excludes a bimolecular decay process of two 360 nm transients. Therefore, the 360 nm transient cannot realistically be assigned to a free radical which decays homogeneously by a bimolecular reaction with another radical.

(5) The rate constants for quenching of triplet sensitizers by azulene are close to the diffusion-controlled limit and are independent of the nature of the sensitizers (Tables 2 and 3). This result is in accordance with fully diffusion-controlled quenching by azulene in the case of indeno[2,1-a]indene as the triplet donor [5]. Transfer of triplet energy is therefore the most plausible explanation for the quenching mechanism, in agreement with previous work [1 - 4]. Thus we conclude that the 360 nm transient is a triplet state of azulene.

Formation and decay of the observed azulene triplet can be described by the following equations.

$$^3S^* + {^1Az} \xrightarrow{k_{az}} {^1S} + {^3Az^*}$$

$$- \frac{d[^3Az^*]}{dt} = (\tau_{az}^{-1} + k_Q[Q])[^3Az^*] + k_s[^3Az^*]^2$$

Here S represents the sensitizer molecule, $k_s$ is the second-order rate constant for triplet–triplet annihilation and $k_Q$ is the pseudo-first-order rate constant for quenching $^3Az^*$ by Q, which represents $^1Az$ (self-quenching) and additives, e.g. oxygen ($k_Q = k_{ox}^{360}$) or impurities. Since the observed triplet lifetime may be reduced by these processes, $\tau^{360}$ represents a lower limit for the lifetime of $^3Az^*$ ($\tau_{az}$). It should be noted that a triplet lifetime of shorter than 1.5 $\mu s$ has been estimated from steady state measurements [3].

The question remains whether the observed azulene triplet is the lowest triplet state since Rentzepis [12] has reported a triplet lifetime of 1 $\mu s$ at 77 K from phosphorescence measurements. As Herkstroeter [4] has already pointed out, either the phosphorescence observed by Rentzepis may correspond to a transition other than $T_1 \to S_0$ or the lowest triplet state is inefficient in accepting energy from the triplet donors. In the latter case, which we believe to be unlikely, the triplet observed in our work is not the lowest azulene triplet.

Absorption of the triplet state of azulene has probably not been observed earlier for the following reasons.

(i) Direct excitation of azulene yields almost no triplet owing to the inefficiency of intersystem crossing [14, 19, 20, 23, 32].

(ii) The triplet lifetime under sensitized excitation conditions is shorter than the time resolution of a conventional flash photolysis apparatus.

(iii) The triplet state of azulene absorbs in a range where many sensitizers show ground state and/or triplet–triplet absorption.

For the last two reasons the triplet state of azulene is observable only using a short excitation pulse and sufficiently high azulene concentrations, i.e. $k_{az}[Az] > (\tau^{360})^{-1}$.

## Acknowledgment

## References

1  W. R. Ware, J. Chem. Phys., 37 (1962) 923.
2  A. A. Lamola, W. G. Herkstroeter, J. C. Dalton and G. S. Hammond, J. Chem. Phys., 42 (1965) 1715.
3  M. Glandien and P. Kröning, Z. Phys. Chem. (Frankfurt am Main), 71 (1970) 149.
   P. Kröning, Z. Phys. Chem. (Frankfurt am Main), 86 (1973) 225.

4 W. G. Herkstroeter, *J. Am. Chem. Soc.*, *97* (1975) 4161.

5 J. Saltiel, P. T. Shannon, O. C. Zafiriou and A. K. Uriarte, *J. Am. Chem. Soc.*, *102* (1980) 6799.

6 J. Saltiel, A. Marinari, D. W.-L. Chang, J. C. Mitchener and E. D. Megarity, *J. Am. Chem. Soc.*, *101* (1979) 2982, and references cited therein.
J. Saltiel and J. L. Charlton, in P. de Mayo (ed.), *Rearrangements in Ground and Excited States*, Vol. 3, Academic Press, New York, 1980, p. 25.

7 H. Görner and D. Schulte-Frohlinde, *Ber. Bunsenges. Phys. Chem.*, *81* (1977) 713.
D. Schulte-Frohlinde and H. Görner, *Pure Appl. Chem.*, *51* (1979) 279.
H. Görner, *J. Photochem.*, *13* (1980) 269.

8 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, in the press.

9 D. G. Whitten and Y. J. Lee, *J. Am. Chem. Soc.*, *94* (1972) 9142.

10 J. Saltiel and D. W. Eaker, *Chem. Phys. Lett.*, *75* (1980) 209.

11 R. Pariser, *J. Chem. Phys.*, *25* (1956) 1112.
F. Fratev, G. Hiebaum and A. Gochev, *Chem. Phys. Lett.*, *16* (1972) 349.
O. C. Hofer and R. M. Hedges, *Chem. Phys. Lett.*, *6* (1970) 67.
J. Pancir and R. Zahradnik, *J. Phys. Chem.*, *77* (1973) 114, 121.

12 P. M. Rentzepis, *Chem. Phys. Lett.*, *3* (1969) 717.

13 D. F. Eaton, T. R. Evans and P. A. Leermakers, *Mol. Photochem.*, *1* (1969) 347.

14 H. J. Griesser and U. P. Wild, *Chem. Phys.*, *52* (1980) 117; *J. Photochem.*, *12* (1980) 115; *J. Chem. Phys.*, *73* (1980) 4715.

15 R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, *67* (1971) 1904.

16 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.

17 A. Garner and F. Wilkinson, *Chem. Phys. Lett.*, *45* (1977) 432.

18 L. K. Patterson, G. Porter and M. R. Topp, *Chem. Phys. Lett.*, *7* (1970) 612.

19 S. Murata, C. Iwanaga, T. Toda and H. Kokubun, *Chem. Phys. Lett.*, *13* (1972) 101; *Ber. Bunsenges. Phys. Chem.*, *76* (1972) 1176.

20 G. Eber, F. Grüneis, S. Schneider and F. Dörr, *Chem. Phys. Lett.*, *29* (1974) 397.
G. Eber, S. Schneider and F. Dörr, *Chem. Phys. Lett.*, *52* (1977) 59.

21 Y. Hirata and E. C. Lim, *J. Chem. Phys.*, *69* (1978) 3292.

22 B. Nickel, *Chem. Phys. Lett.*, *68* (1979) 17.

23 J. B. Birks, *Chem. Phys. Lett.*, *17* (1972) 370.
N. J. Turro, V. Ramamurthy, W. Cherry and W. Farneth, *Chem. Rev.*, *78* (1978) 125.

24 A. Garner and F. Wilkinson, *J. Chem. Soc., Faraday Trans. II*, *72* (1976) 1010.

25 G. Porter and M. A. West, in A. Weissberger (ed.), *Techniques of Chemistry*, Vol. VI/2, Wiley, New York, 1974, p. 367.
J. W. Hilpern, G. Porter and L. J. Stief, *Proc. R. Soc. London, Ser. A*, *277* (1964) 437.
K. H. Grellmann and H.-G. Scholz, *Chem. Phys. Lett.*, *62* (1979) 64.

26 A. Farmilo and F. Wilkinson, *Chem. Phys. Lett.*, *34* (1975) 575.

27 A. J. Fry, R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, *88* (1966) 4781.

28 M. Kikuchi, K. Kikuchi and H. Kokubun, *Bull. Chem. Soc. Jpn.*, *47* (1974) 1331.

29 A. Gilbert, J. M. Kelly and E. Koerner von Gustorf, *Mol. Photochem.*, *6* (1974) 225.

30 A. P. Chapple, J. P. Vikesland and F. Wilkinson, *Chem. Phys. Lett.*, *50* (1977) 81.

31 J. Saltiel and B. Thomas, *Chem. Phys. Lett.*, *37* (1976) 147.
O. L. J. Gijzeman, F. Kaufman and G. Porter, *J. Chem. Soc., Faraday Trans. II*, *69* (1973) 708.

32 E. P. Ippen, C. V. Shank and R. L. Woerner, *Chem. Phys. Lett.*, *46* (1977) 20.
C. V. Shank, E. P. Ippen, O. Teschke and R. L. Fork, *Chem. Phys. Lett.*, *57* (1978) 433.