# THE TRIPLET STATE ENERGIES OF RUBRENE AND DIPHENYLISO-BENZOFURAN

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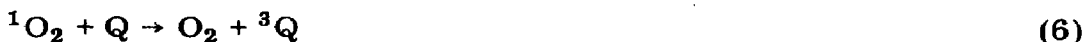*Research Laboratories, Eastman Kodak Company, 1669 Lake Avenue, Rochester, NY 14650 (U.S.A.)*

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## Summary

Until now controversies have arisen from the estimates of the triplet energies of rubrene (R) and diphenylisobenzofuran (DPBF), both of which are known reactants with singlet oxygen. To clarify the situation, flash kinetic spectroscopy was used to measure rates of energy transfer between these two molecules and other energy donor and energy acceptor molecules of known triplet energy. The lowest excited triplet state in R is nearly isoenergetic with the corresponding state in zinc phthalocyanine, and the energy value assignment is $9.2 \pm 0.2$ kilokaysers. Triplet–triplet annihilation is thermoneutral and is consistent with the lowest triplet state having approximately one-half the energy of the lowest excited singlet state. Based on the rates at which azulene and ferrocene quench the lowest excited triplet state of DPBF, the energy of this state can be assigned a value of $11.9 \pm 0.1$ kilokaysers.

## 1. Introduction

Both rubrene (R) and diphenylisobenzofuran (DPBF) are widely used as singlet oxygen substrates to measure quantum yields of singlet oxygen production as well as the effectiveness of singlet oxygen quenchers [1 - 16]. These substrates both react cleanly to form photoperoxides according to the following reaction scheme. This reaction scheme is described in terms of R but also applies to DPBF.

$$R \xrightarrow{h\nu} {}^1R \tag{1}$$

$${}^1R + O_2 \rightarrow {}^3R + {}^1O_2 \; (O_2) \tag{2}$$

$${}^3R + O_2 \rightarrow R + {}^1O_2 \tag{3}$$

$${}^1O_2 \rightarrow O_2 \tag{4}$$

$${}^1O_2 + R \rightarrow RO_2 \tag{5}$$

$${}^1O_2 + Q \rightarrow O_2 + {}^3Q \tag{6}$$

$$^3R + Q \rightarrow R + {}^3Q \tag{7}$$

$$^3Q \rightarrow Q \tag{8}$$

Here Q represents an added quencher and the superscripts represent the excited states involved.

Rubrene has also found application as a chemiluminescent reagent for monitoring the progress of electrochemical reactions [17 - 25]. Here A represents an appropriate electron acceptor and D represents an electron donor.

$$D \rightarrow D^{\cdot +} + e^- \tag{9}$$

$$A + e^- \rightarrow A^{\cdot -} \tag{10}$$

These radical ions can be generated either photochemically or electrochemically. Reaction between the radical ions can occur provided that the acceptor has a less positive potential than the donor radical cation.

$$D^{\cdot +} + A^{\cdot -} \rightarrow {}^3D + A \tag{11}$$

$$D^{\cdot +} + A^{\cdot -} \rightarrow D + {}^3A \tag{12}$$

In eqns. (9) - (12) R can be the electron donor or this role may be filled by another compound. If R is the donor, then $^3R$ can be generated in eqn. (11). Otherwise R can intercept $^3A$ by energy transfer as in

$$^3A + R \rightarrow A + {}^3R \tag{13}$$

$$2\,^3R \rightarrow {}^1R + R \tag{14}$$

$$^1R \rightarrow R + h\nu \tag{15}$$

In this mechanism of triplet–triplet annihilation [26, 27], it has been questioned whether the triplet of R is sufficiently energetic to undergo annihilation leading to $^1R$ and subsequent fluorescence [18]. If $^3R$ does indeed have insufficient energy for eqn. (14), then an alternative path for the generation of $^1R$ must be considered. (The spin statistical factor limits the rate of production of fluorescent $^1R$ to one-ninth of that for the overall rate of triplet–triplet annihilation [28].)

Knowledge of the energy of the lowest excited triplet state of luminescent and/or reactive molecules can be important in mechanistic interpretations of photophysical processes and photochemical reactions. However, experimental determinations of the precise triplet energies of R and DPBF have yielded different values in the hands of different experimentalists. Yildiz *et al.* [29] reported that benzophenone and biacetyl sensitized the formation of $^3R$ but that 9-anthraldehyde and tetracene did not; accordingly, these authors concluded that $^3R$ would be bounded between the triplet energies of biacetyl and 9-anthraldehyde (19.5 and 14.6 kilokaysers respectively). By contrast, the degree of the inhibition of R photooxidation by azulene as measured by Algar and Stevens [1] would place the triplet state of R below 13.7 kilokaysers. Stevens and Ors [9] report that the $\beta$ value for R is approximately $1 \times 10^{-3}$, which means that it does not effectively

quench singlet molecular oxygen and, as such, the triplet state of R must be more energetic than 7.9 kilokaysers. On the basis of electron acceptors as quenching agents for $^3$R, Liu and Faulkner [24] have placed bounds on the R triplet energy between 1.04 and 1.29 eV (8.4 and 10.4 kilokaysers). A more precise estimate of the R triplet energy at 9.3 ± 0.3 kilokaysers is given by Liu and Faulkner and is based on electron transfer quenching, but, as they point out, this value is somewhat suspect because of the complexity of the quenching reactions.

In electrochemical reactions the fluorescence exhibited by R has been attributed to the lowest excited singlet state of R generated by triplet–triplet annihilation, according to eqns. (14) and (15). Visco and Chandross [18] have questioned whether $^3$R has sufficient energy to generate the fluorescent singlet state. Certainly, there would be no problem in rationalizing this mechanism if the triplet state of R had the energy proposed by Yildiz *et al.* [29]. R can be regarded as a derivative of tetracene, whose triplet energy is 10.2 kilokaysers [30]. We must consider whether phenyl substitution in tetracene raises or lowers the triplet energy. Ting's calculations indicate that substitution of this type raises the triplet energy level relative to the parent molecule [31], but Brinen and Koren [32] have convincing experimental evidence that the opposite is true. If $^3$R is less energetic than triplet tetracene, the annihilation process leading to the fluorescent singlet state is problematical, according to Visco and Chandross [18]. This point of view is supported by the experiments of Dreeskamp and coworkers [33, 34], who showed that the rate of quenching of R fluorescence by iodopropane is consistent with an S–T splitting in R of about 10.9 kilokaysers with no higher excited triplet states located in this energy gap; this energy separation would place the $T_1$ state near 8.0 kilokaysers. Kusuhara and Hardwick [35] claim that the triplet of R in benzene solution decays by a first-order process with no second-order contribution. By contrast, Liu and Faulkner [24] claim that R does undergo triplet–triplet annihilation and that the process is thermoneutral.

There are also conflicting claims concerning the triplet energy of DPBF. Weishaupt *et al.* [36] have reported phosphorescence from DPBF in ethanol-ether at liquid nitrogen temperature; this phosphorescence placed the DPBF triplet at 21.8 kilokaysers above the ground state. Singh *et al.* [37] believe that this claimed phosphorescence must really be fluorescence and present experimental evidence to bracket the triplet of DPBF between those of tetracene (10.2 kilokaysers) [30] and $\beta$-carotene (7.7 kilokaysers) [38]. This experimental evidence is based on energy transfer measurements in which it is claimed that DPBF quenches triplet tetracene but does not quench triplet $\beta$-carotene. This energy assignment of the triplet state of DPBF is inconsistent with the measurement of Merkel and Kearns [5], who noted that DPBF did not efficiently quench the triplet state of methylene blue by energy transfer; this fact would place the triplet of DPBF above 11.5 kilokaysers. Ziebig and Pragst [39] assign an energy value of 12.9 ± 0.4 kilokaysers to the DPBF triplet, based on sensitized electrogenerated chemiluminescence experiments as well as the minimal enthalpy of luminescent electron transfer.

To utilize R and DPBF optimally in photochemical experiments, knowledge of the energies of their triplet states is essential. Because of uncertainties in the energies of the triplets of both molecules, experiments were carried out to resolve the situation. These experiments involve triplet energy transfer either from a sensitizer to R or DPBF or from these substrates to added quenchers. The triplet energy donors and acceptors selected for these experiments have triplet states whose energies have been measured previously. Lamola [40] has noted the utility of the energy transfer method for triplet energy determination and that it is the method of choice when other methods fail or give equivocal results.

## 2. Results and discussion

Initially, experiments were run to see whether the triplets of R and DPBF could be observed directly in degassed solution immediately after flash excitation. Triplet–triplet absorption was observed after direct excitation of R but not from direct excitation of DPBF, and these observations confirm reports in the literature [29, 37]. On addition of an appropriate triplet sensitizer (such as 10,10-dimethylanthrone [41]) to these R and DPBF solutions, the intensity of triplet–triplet absorption of R is strengthened and such absorption first becomes observable in DPBF. This behavior also confirms reports in the literature [29, 37, 42].

The observation of triplet–triplet absorption in a compound does not provide a direct measurement of triplet energies but provides a means of monitoring rates of energy transfer. Energy transfer reactions involving R and DPBF were monitored according to the schemes

$$^3S + R \rightarrow S + {}^3R \tag{16}$$

$$^3R + Q \rightarrow R + {}^3Q \tag{17}$$

Here S stands for sensitizer or energy donor and Q stands for quencher or energy acceptor. These equations are written in terms of R but apply equally well to DPBF. In contrast with many compounds with short-lived triplets whose triplet energies were determined by energy transfer experiments in earlier studies, both R and DPBF have triplets that are sufficiently long lived to make reversible energy transfer feasible when the energy donors and energy acceptors of eqns. (16) and (17) are approximately isoenergetic.

Initial experiments were run with R to see how effectively this compound quenched sensitizers whose triplets spanned a broad range in energy. Table 1 is a list of the measured rate constants for energy transfer from those sensitizers which, in their lowest excited triplet states, transferred energy to R independently of sensitizer concentration and at a diffusion-limited rate. This means that the energy gap between the sensitizer and $^3R$ is sufficiently large that reverse energy transfer to the sensitizer from $^3R$ does not occur at a measurable rate. The sensitizers that meet this criterion must have triplets

TABLE 1

Rate constants $k_q$ for quenching of triplet sensitizers by rubrene in benzene solution

| Sensitizer | Sensitizer $E_T$ (kilokaysers) | $k_q$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|
| 1,2,5,6-Dibenzanthracene | 18.3[a] | $2.2 \times 10^9$ |
| 1,2-Benzanthracene | 16.5[a] | $1.8 \times 10^9$ |
| Anthracene | 14.9[b] | $2.8 \times 10^9$ |
| 3,4,9,10-Dibenzpyrene | 14.1[c] | $1.7 \times 10^9$ |
| Anthanthrene | 11.8[c] | $1.6 \times 10^9$ |

[a]Data taken from ref. 43.
[b]Data taken from ref. 44.
[c]Data taken from ref. 45.

at least 1.0 kilokayser more energetic than $^3$R. From these data we can conclude that $^3$R must be below 11.0 kilokaysers in energy.

Two other sensitizers were tried with rubrene: violanthrene and zinc phthalocyanine (ZnPc). The triplet of violanthrene was not measurably quenched by R, whereas the triplet of ZnPc was quenched. However, the measured rate of decay of $^3$ZnPc in the presence of R was dependent on the concentration of the sensitizer and provided evidence that reverse energy transfer from $^3$R to ZnPc was taking place. For this to occur, the triplet states of ZnPc and R must be within 1.0 kilokayser of each other. The triplet energy of ZnPc is known to be 9.1 kilokaysers [46]. The failure of R to quench the violanthrene triplet places $^3$R at least 1.0 kilokayser above the triplet of violanthrene at 8.0 kilokaysers [47]. On this basis $^3$R can be bounded between 9.0 and 10.1 kilokaysers.

Further refinements in the determination of the energy of $^3$R were made in a more thorough investigation of the reversible energy transfer reactions that ZnPc and R undergo in their triplet states. These refinements are based on a measurement of the equilibrium

$$^3ZnPc + R \rightleftharpoons ZnPc + {}^3R \tag{18}$$
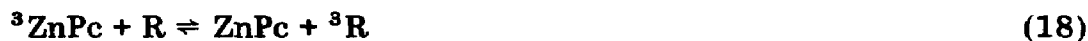
by the technique of Kira and Thomas [48]. Applications of this technique require knowledge of the extinction coefficients for triplet–triplet absorption at two different wavelengths for each of the two substances. The absorbance of the triplet–triplet absorption signal must be measured at these two wavelengths at the same time interval after the excitation flash that generates the triplets. From these measurements the individual concentrations of $^3$R and $^3$ZnPc can be determined. To check the precision of such determinations, the measurements should be repeated with different starting concentrations of R and ZnPc.

The two wavelengths selected for monitoring the combined absorption of $^3$R and $^3$ZnPc are 450 and 545 nm. Absorption by $^3$ZnPc occurs at both wavelengths but $^3$R absorbs only at 450 nm, so the evaluation of the individual triplet concentrations of R and ZnPc is simplified.

The extinction coefficient for triplet–triplet absorption in R at 450 nm was determined by the method of Land [49], in which a known concentra-

TABLE 2

Experimentally determined extinction coefficients
for triplet–triplet absorption

| Substance | $\lambda$ (nm) | $\epsilon$ (M$^{-1}$ cm$^{-1}$) |
|---|---|---|
| R | 450 | $3.0 \times 10^3$ |
| ZnPc | 450 | $5.1 \times 10^4$ |
| ZnPc | 545 | $4.4 \times 10^4$ |

TABLE 3

Equilibrium constants for reversible triplet energy
transfer between R and ZnPc according to eqn. (18) at
different starting concentrations of these molecules

| [R] (M) | [ZnPc] (M) | $K$ |
|---|---|---|
| $5.0 \times 10^{-6}$ | $5.0 \times 10^{-6}$ | 0.39 |
| $1.2 \times 10^{-5}$ | $5.0 \times 10^{-6}$ | 0.79 |
| $5.0 \times 10^{-6}$ | $1.0 \times 10^{-5}$ | 0.30 |
| $5.0 \times 10^{-6}$ | $2.0 \times 10^{-6}$ | 0.94 |
| $1.5 \times 10^{-5}$ | $8.0 \times 10^{-6}$ | 0.86 |
| $1.0 \times 10^{-5}$ | $1.0 \times 10^{-5}$ | 0.53 |
| $3.0 \times 10^{-5}$ | $3.0 \times 10^{-5}$ | 1.07 |

tion of benzophenone was used with sufficient R for total quenching of the
flash-generated benzophenone triplet state. The excited state extinction
coefficients for ZnPc were measured by another method applicable to mole-
cules whose triplet states undergo triplet–triplet annihilation efficiently [50].
Table 2 is a list of these extinction coefficients.

With this information, we determined the equilibrium constant $K$ for
eqn. (18) for a series of solutions of different starting concentrations of R
and ZnPc (Table 3). The average value of $K$ is 0.7 ± 0.4. The free-energy
change is related to $K$ by

$$-\Delta G = 2.303RT \log K \qquad (19)$$

The difference $\Delta E_T$ in triplet energies between the species in equilibrium is
equal to $-\Delta G$, as has been demonstrated by Kira and Thomas [48]. The
triplet of R can therefore be assigned an energy value of 9.2 ± 0.2 kilokaysers
(1.14 ± 0.02 eV).

Additional energy transfer experiments were run to verify this energy
value assignment for $^3$R. These experiments were based on the rates at
which quenchers of known triplet energy quench $^3$R. Both azulene and
ferrocene, the quenchers selected, have triplet lifetimes that are sufficiently
short to preclude reversible energy transfer of the type shown in eqn. (18)
[38]. Azulene, even at a concentration as high as $1 \times 10^{-3}$ M, was ineffective

in quenching $^3$R. In this respect azulene contrasts sharply with ferrocene. We measured the rate constant for energy transfer from $^3$R to ferrocene to be $2.8 \times 10^7$ $M^{-1}$ $s^{-1}$. Previously, the rate constant for energy transfer from $^3$ZnPc to ferrocene had been measured as $2.6 \times 10^7$ $M^{-1}$ $s^{-1}$ [38]. Because the energy of $^3$ZnPc is known precisely [46] and because ferrocene quenches $^3$R slightly more efficiently than $^3$ZnPc does (whereas azulene quenches neither), it follows that $^3$R must be slightly more energetic than $^3$ZnPc.

Some comments should be made about triplet–triplet annihilation of $^3$R. Strickler and Berg [51] have published absorption and fluorescence spectra of R. The energy of the lowest excited singlet state of R is equal to the energy of the 0–0 band in these spectra; the 0–0 band is the cross-over point in the spectral profiles and has a value of $18.5 \pm 0.2$ kilokaysers. Pragst [22] claims a singlet energy for R that is 0.7 kilokayser less than this value. The assigned triplet energy value for R together with this value for the lowest excited singlet state means that triplet–triplet annihilation of $^3$R to produce $^1$R is energetically feasible. This conclusion was verified with a measured rate constant of $1.1 \times 10^8$ $M^{-1}$ $s^{-1}$ for $^3$R–$^3$R annihilation. No temperature dependence of this rate constant was observed over the range 15 - 53 °C. Our first-order decay rate constant for $^3$R of $(8.7 \pm 0.2) \times 10^3$ $s^{-1}$ matches previously published values [29, 42]. The conclusions are that triplet–triplet annihilation in R (1) is feasible, (2) can be measured and (3) is thermoneutral.

The determination of the energy of $^3$DPBF was undertaken by re-investigating some previously reported claims involving energy transfer and DPBF. In contrast with the claim by Singh *et al.* [37], we found that DPBF does not quench triplet tetracene with an energy of 10.2 kilokaysers, at least not with a DPBF concentration in degassed benzene solution of $2.1 \times 10^{-5}$ M; Singh *et al.* [37] did not report their experimental conditions. We also support the claim of Merkel and Kearns [5], dismissed by Singh *et al.* [37] solely on the basis of their triplet tetracene result, that DPBF does not quench triplet methylene blue with an energy of 11.5 kilokaysers. It follows that $^3$DPBF must be higher in energy than triplet methylene blue is.

Azulene, ferrocene and *trans*-stilbene were selected as quenchers and the rate constants with which they accept energy from $^3$DPBF were measured. Because direct excitation of DPBF does not yield a measurable quantity of $^3$DPBF an additional sensitizer, 10,10-dimethylanthrone, was added to the experimental solutions. The 10,10-dimethylanthrone produces triplets effectively but itself shows no triplet–triplet absorption to interfere with the monitoring of $^3$DPBF at 720 nm. The rate constant for first-order deactivation of $^3$DPBF in benzene in the absence of added quenchers is $1.85 \times 10^3$ $s^{-1}$; there is also a second-order component in the $^3$DPBF deactivation, which is attributable to triplet–triplet annihilation. Because the triplets of the three quenchers are too short lived for direct observation [38, 52], only $^3$DPBF was observable in the experimental solutions. For quenching of $^3$DPBF, *trans*-stilbene, with a triplet energy greater than 17 kilokaysers [53], proved to be ineffective, whereas both azulene and ferrocene yielded measurable rate constants. Rather significantly, the rate constants for azulene and ferrocene

TABLE 4

Rate constants for energy transfer to azulene and ferrocene in benzene solution

| Energy donor | Azulene $k_q$ ($M^{-1}$ $s^{-1}$) | Ferrocene $k_q$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|
| 3,4,8,9-Dibenzpyrene | $9.0 \times 10^7$ [a] | $6.8 \times 10^8$ [a] |
| DPBF | $6.5 \times 10^7$ [b] | $6.1 \times 10^8$ [b] |
| Anthanthrene | $5.6 \times 10^7$ [a] | $4.8 \times 10^8$ [a] |

[a]Data taken from ref. 38.
[b]This work.

quenching of two sensitizers with known triplet energies bracket the measured rate constants for $^3$DPBF quenching. These two sensitizers are 3,4,8,9-dibenzpyrene and anthanthrene and have triplet energies of 12.0 kilokaysers and 11.8 kilokaysers respectively [45]. The experimental rate constants are summarized in Table 4. As the triplet energies of these two sensitizers differ by only 0.2 kilokaysers, the energy of $^3$DPBF can be assigned a value of 11.9 ± 0.1 kilokaysers.

All discussion to this point is based on energy transfer as in eqns. (16) and (17) to account for deactivation of all excited triplet states. The deactivation of excited triplet states by electron transfer, the reverse of eqns. (11) and (12), should be considered. For example, it is known that ferrocene [54] and rubrene [17 - 25] can be involved in electron transfer reactions. The relative contributions of electron transfer and energy transfer in our experiments can be ascertained by applying the Weller equation for measuring $\Delta G$ values of electron transfer reactions [54 - 56]. In so far as the oxidation and reduction potentials were available, the Weller equation was applied to all possible donor–acceptor combinations used experimentally here. In no case was the $\Delta G$ value less endothermic than 0.5 eV and many donor–acceptor combinations yielded $\Delta G$ values that were twice as large as this value. Furthermore, the oxidation and reduction potentials are based on measurements in relatively polar solvents such as acetonitrile and dimethylformamide. Electron transfer reactions are known to be facilitated in polar solvents relative to non-polar solvents [57 - 59] so that, if electron transfer reactions are unlikely in acetonitrile and dimethylformamide, these reactions must be even less likely in benzene, our solvent for the experiments.

Some comments on the earlier reported phosphorescence of DPBF [35] seem to be appropriate. Luminescence with a 0–0 band at 458 nm (21.8 kilokaysers) from DPBF in a mixture of ethanol and ether at 77 K had been identified as phosphorescence. We have reinvestigated this luminescence and, as proposed by Singh et al. [37], it is fluorescence rather than phosphorescence. What is unusual about this fluorescence, however, is that its lifetime is so long that it can be observed even with a rotating-can phosphoroscope. With other solvents such as 2-methyltetrahydrofuran, hydrocarbon mixtures or ethanol–ether with added heavy atom components, the fluorescence lifetime of DPBF is sufficiently shortened that no luminescence is observed with the rotating-can phosphoroscope.

The lowest energy absorption band observed in DPBF is quite intense with an extinction coefficient of $2.3 \times 10^4$ $M^{-1}$ $cm^{-1}$. For an extinction coefficient this large, the expected fluorescence lifetime would be about 5 ns [51, 60]. The rotating-can phosphoroscope, however, should eliminate all luminescence that is shorter lived than 1 ms. It appears that in ethanol–ether DPBF luminesces from a state to which direct excitation from the ground state is forbidden. It is of course possible that the alcohol in the solvent induces shifts in energies of one or more states to make the "forbidden" state the lowest energy excited singlet state. The exact nature of excited singlet states of DPBF and their possible solvent-induced shifts in energy are not the subject of this paper but remain as subjects for future detailed investigations.

## 3. Conclusions

The energies of $^3$R and $^3$DPBF, as determined by energy transfer methods, are $9.2 \pm 0.2$ kilokaysers and $11.9 \pm 0.1$ kilokaysers respectively. Both of these substrate molecules for $^1O_2$ have discernible triplet–triplet absorption spectra and readily measurable lifetimes in degassed benzene solutions. For R the triplet–triplet absorption spectrum can be observed after direct excitation but with DPBF this does not occur; observation of triplet–triplet absorption in DPBF requires indirect excitation of this molecule by energy transfer from a triplet sensitizer of appropriate energy. Triplet–triplet annihilation can occur in R and is thermoneutral at temperatures near ambient temperature. An unusually long-lived fluorescence is exhibited by DPBF when this molecule is contained in an ethanol–ether host mixture at liquid nitrogen temperature.

## 4. Experimental section

### 4.1. Materials

The rubrene was Eastman reagent grade and was used as received. The diphenylisobenzofuran was from Aldrich and was recrystallized from a mixture of acetone and water. The zinc phthalocyanine was Eastman reagent grade and was recrystallized from pyridine. The preparation and purification of 10,10-dimethylanthrone have been described elsewhere [41]. The *trans*-stilbene used in these experiments had been zone refined and was purchased from James Hinton. The tetracene was Eastman reagent grade and was recrystallized from xylene. The sources and purification of the remaining sensitizers have been described elsewhere [38]. The benzene was Mallinckrodt Nanograde and was used as received.

### 4.2. Procedures

All measurements of triplet–triplet absorption and of energy transfer were made on a flash photoelectric apparatus. Two xenon flashlamps

(Kemlite Z8H20) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inner walls were coated with highly reflective paint (Eastman white reflectance coating). The flash discharge energy was 156 J, corresponding to a 2 $\mu$F capacitor charged to 12.5 kV. Glass color filters (Corning 9863) were placed between the flashlamps and the sample cell holder. The monitoring source was a quartz–halide 100 W lamp (Osram 64625) powered by a regulated d.c. power supply (Sorensen QSB12-8). The lamp was mounted in an appropriate housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens and a monochromator 0.25 m long (Jarrell Ash). The monitoring beam, after passing through the sample cell, was focused on the entrance slit of the monochromator. Light intensity as a function of time was measured by means of a photomultiplier tube (RCA4463) located at the exit slit of the monochromator. The output from the photomultiplier was fed into a cathode follower amplifier and then into a wide-band digital storage oscilloscope (Nicolet model 1090). The output voltage of the photomultiplier, read directly in digital form on the oscilloscope screen as a function of time, was linear with regard to the light intensity transmitted by the sample, so that an observed change in voltage after flash excitation could be readily converted mathematically to a change in absorbance in the sample. Transient lifetimes were measured by the recovery rate of the monitoring beam after the excitation flash. The kinetic analysis was by the method of Linschitz and Sarkanen [61, 62].

The cylindrical Pyrex glass sample cells were 25 cm long and had an outside diameter of 15 mm with flat windows fused to the ends. The cells were connected by side arms to bulbs in which solutions were contained during degassing. Solutions were degassed by subjecting them to several freeze–pump–thaw cycles on a high vacuum manifold before the sample containers were sealed.

The procedures for luminescence measurements have been described elsewhere [63].

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