Photophysical triplet state processes of 4-H-1-benzopyrane-4-thione in a perfluoroalkane

Part 1.—Temperature dependence of unimolecular triplet decay

Heike Eisenberger and Bernhard Nickel*

Max-Planck-Institut für Biophysikalische Chemie, Abteilung Spektroskopie und Photochemische Kinetik, Am Fassberg 11, D-37077 Göttingen, Federal Republic of Germany

The rate constant k_1^0 for the unimolecular decay of the lowest triplet state, T_1 , of 4-H-1-benzopyrane-4-thione (BPT) in perfluoro-1,3-dimethylcyclohexane was determined between 230 and 300 K. By assuming a very fast and virtually complete thermal equilibration $T_1 \rightleftharpoons S_1$ of the relative population of T_1 and the lowest excited singlet state S_1 , three parameters can be calculated from the temperature dependence of k_1^0 : the individual rate constants $\beta_s = (4.0 \pm 0.2) \times 10^6 \text{ s}^{-1}$ for the decay of S_1 to S_0 and $\beta_T^z = (8.2 \pm 2) \times 10^4 \text{ s}^{-1}$ for the decay of the strongly phosphorescent triplet substate T_1^z to S_0 , and the energy difference $\Delta E(S_1, T_1^z) = hc$ $\times (757 \pm 13) \text{ cm}^{-1}$ between T_1^z and S_1 . The value of $\Delta E(S_1, T_1^z)$ is in agreement with the positions of $T_{1,0}$ and $S_{1,0}$ in the absorption spectrum. The spectrum of the $S_0 \rightarrow S_1$ transition is estimated.

The assignment of the hot-band range of the delayed luminescence above the energy $hc\tilde{v}_{0,0}$ of $T_{1,0}$ is facilitated by an inverse Boltzmann weighting (multiplication with $\exp[hc(\tilde{v} - \tilde{v}_{0,0})/k_BT]$). At the position of $S_{1,0}$, a contribution of E-type delayed $S_1 \rightarrow S_0$ fluorescence can be discerned.

The contribution of diffusion-controlled concentration-quenching (rate constant k_Q) to the triplet decay was eliminated by extrapolation to infinite dilution; k_Q is proportional to the ratio T/η of temperature T and viscosity η . The temperature dependence of the viscosity and density of perfluoro-1,3-dimethylcyclohexane were measured.

Introduction

Aromatic thiocarbonyl compounds (thiones) have unusual photophysical and photochemical properties, which have been the subject of many investigations.¹ Nevertheless, several questions of principal interest have remained unanswered, and in this article and in two following ones^{2,3} we try to answer some of them. 4-H-1-Benzopyran-4-thione (BPT) was chosen as a representative thione for reasons that will become evident later. A perfluoroalkane was chosen as solvent,⁴ because the perfluoroalkanes are the only known class of compounds that behave as inert solvents for the present purpose. In the following we first itemize the known photophysical and photochemical properties of thiones in general and of BPT in particular and then present the objectives of this investigation.

Photophysical and photochemical properties of thiones

(i) The spin-forbidden transition $S_0 \rightarrow T_1$ from the electronic ground state S_0 to the lowest triplet state T_1 is unusually strong (see Fig. 1 and 2). Under the experimental conditions of the present investigation, the phosphorescence $T_1 \rightarrow S_0$ is the strongest observable emission from BPT in a fluid solvent at room temperature (see Fig. 2).

(*ii*) The zero-field splitting in T_1 is very large.⁵ In BPT the triplet substate T_1^z lies *ca.* 20 cm⁻¹ above the substates T_1^x , T_1^y , which are separated by only 0.06 cm⁻¹.⁶ Therefore substate-specific triplet state properties have to be taken into account at rather high temperatures.

(*iii*) The lowest triplet state of thiones is quenched by ground-state molecules of the same kind (concentration quenching[†]) in a diffusion-controlled reaction.⁷ The quen-

ching process is at least in part a chemical reaction, as seen by the formation of unstable and stable photoproducts.⁸

(*iv*) The energy gap between T_1 and S_1 is unusually small (*ca.* $hc \times 750 \text{ cm}^{-1}$) and the transition $S_0 \rightarrow S_1$ is very weak (about as weak as the transition $S_0 \rightarrow T_1$).⁹ As a consequence, a separate $S_0 \rightarrow S_1$ absorption band is not observed, and the energy of S_1 is to some degree uncertain (see the right part of the absorption spectrum in Fig. 2).

(v) Intersystem crossing $S_1 \rightarrow T_1$ is much faster than the individual, radiative and non-radiative decays of S_1 and T_1 to the ground state.¹⁰ There is no identifiable prompt $S_1 \rightarrow S_0$ fluorescence.¹ The rate constant β_{S_1} for the radiative and non-



Fig. 1 Observable radiative transitions (---) and postulated nonradiative transitions (---) of BPT in a perfluoroalkane. The numbers in parentheses are energies in units of cm⁻¹ and refer to BPT in PF-1,3-DMCH (with the exception of the value of |D|/hc for BPT in *n*-hexane). The rate constants β are sums of the respective radiative and non-radiative decay rate constants. Abbreviations: DF: delayed fluorescence; IC: internal conversion; ISC: intersystem crossing, P: phosphorescence; PF: prompt fluorescence; VR: vibrational relaxation.

[†] In the literature the term 'self-quenching' is widely used. In our opinion, this is a misnomer in two respects. First, the term self-quenching would really make sense if applied to triplet-triplet annihilation; but this use has not been customary. Secondly, in particular in connection with the quenching of inherently long-lived states, the true quencher in concentration quenching is often an impurity; in this case the term 'self-quenching' even implies a wrong statement.



Fig. 2 Absorption spectrum $\epsilon(\lambda)$ (----) and spectrum of prompt luminescence (---) (S₂ \rightarrow S₀ fluorescence and T₁ \rightarrow S₀ phosphorescence) of BPT in PF-1,3-DMCH at room temperature

radiative decay of S_1 to S_0 (cf. Fig. 1) is not accessible to a direct experimental determination.

(vi) An E-Type (thermal) delayed $S_1 \rightarrow S_0$ fluorescence due to thermally activated intersystem crossing $T_1 \rightsquigarrow S_1$ is in principle observable,¹¹ but the distinction between E-type delayed fluorescence and hot bands of the phosphorescence is difficult (similar to the situation with aromatic ketones¹²).

(vii) The most striking property of thiones is a rather large energy gap between S_1 and S_2 . As a consequence, internal conversion $S_2 \rightarrow S_1$ is relatively slow, and a prompt, electricdipole allowed $S_2 \rightarrow S_0$ fluorescence is easily observed^{13,14} (see Fig. 2).

(*viii*) Thiones in their excited electronic states react practically with all common solvents.^{7,8} The only class of compounds that behave as photophysically and photochemically inert solvents are the perfluorinated alkanes.⁴

Objectives of this investigation

Temperature dependence of concentration quenching of T_1 . The main experimental objective of this investigation has been the determination of the rate constant k_T^0 of unimolecular triplet decay in a large temperature range. Due to diffusioncontrolled concentration quenching of T_1 , k_T^0 can be obtained only by linearly extrapolating the measured rate constant k_T in a Stern–Volmer plot to zero solute concentration.^{1,15,16} Thus the first experimental task was the systematic study of concentration quenching in a large temperature range.

Temperature dependence of unimolecular triplet decay. The temperature dependence of k_T^0 can be described by a kinetic model, whose basic feature is a virtually complete equilibration $T_1 \rightleftharpoons S_1$ that is much faster than the individual decays of T_1 and S_1 to S_0 . Let p_T and $p_{S_1} = 1 - p_T$ be the probabilities of an excited BPT molecule being in T_1 or S_1 . Then the relation between the measurable rate constant k_T^0 and the rate constants β_T and β_{S_1} for the individual decays of T_1 and S_1 to S_0 is $k_T^0 = p_T \beta_T + p_{S_1} \beta_{S_1}$. The evaluation of the temperature dependence of k_T^0 yields three quantities: the rate constants β_T and β_{S_1} and the energy difference $\Delta E(T_1, S_1)$ between T_1 and S_1 (see Fig. 1). In a refined treatment, the zero-field splitting of T_1 will be taken into account. The determination of β_S has been of particular interest, since β_{S_1} cannot be reliably determined in any other way.[†]

Distinction between $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ absorption bands. The only directly observable feature of the $S_0 \rightarrow S_1$ absorption band is the 0,0 transition at 600 nm (see Fig. 2). The spectrum of the $S_0 \rightarrow S_1$ absorption band can be obtained by subtracting the $S_0 \rightarrow T_1$ spectrum from the total absorption spectrum between 480 and 660 nm. This will be done with reasonable accuracy by assuming an approximate mirror symmetry between the $T_1 \rightarrow S_0$ phosphorescence spectrum and the $S_0 \rightarrow T_1$ absorption spectrum.

E-type delayed fluorescence. Because of the lack of prompt $S_1 \rightarrow S_0$ fluorescence, the observation of an E-type delayed fluorescence is of particular interest.^{16,17} The assignment of the hot-band range of the delayed luminescence above the energy $h\tilde{v}_{0,0}$ of $T_{1,0}$ is facilitated by an inverse Boltzmann weighting (multiplication by $\exp[hc(\tilde{v} - \tilde{v}_{0,0})/k_BT]]$). It will be shown that an E-type delayed fluorescence can be distinguished from hot phosphorescence bands with the same certainty as a portion of the lowest absorption band of BPT can be assigned to the $S_0 \rightarrow S_1$ transition. In connection with the E-type delayed fluorescence and the interpretation of the temperature dependence of k_T^0 , the agreement between the phosphorescence excitation spectrum and the absorption spectrum will be important. This particular aspect will be treated in ref. 3.

Choice of compounds. The three thiones for which most information has been available are pyranethione (PT), BPT and xanthione (XT). As far as a reliable determination of the rate constant k_T^0 of unimolecular triplet decay is concerned, a short maximal triplet lifetime $\tau_T^0 = 1/k_T^0$ is advantageous, because this automatically reduces the relative contribution of concentration quenching to the total triplet decay. In this respect XT ($\tau_T^0 \approx 8.5 \ \mu s^1$) would be more suitable than PT ($\tau_T^0 \approx 43 \ \mu s^1$) or BPT ($\tau_T^0 \approx 16 \ \mu s^1$). Also with respect to photochemical stability, XT would be the best choice.⁸ The third and indispensable property, however, is a sufficient solubility of the thione in perfluoroalkanes at low temperatures. In this respect PT would be best suited, BPT is acceptable, and XT is out of question. Thus BPT has been a good compromise.

For the solvent, the choice has been between perfluorohexane, perfluoromethylcyclohexane, and perfluoro-1,3dimethylcyclohexane (PF-1,3-DMCH). PF-1,3-DMCH has been best suited in three respects: First, most of the literature data on BPT refer to this solvent. Secondly, for the determination of the unimolecular triplet decay rate constant k_T^0 , PF-1,3-DMCH is most suitable, because it has the highest viscosity of the three solvents. Thirdly, PF-1,3-DMCH is a slightly better solvent than the other two. The only advantage of perfluorohexane would be its lower melting point.⁴

Finally we note a terminological distinction. The prompt luminescence is the total luminescence that is measured in a steady-state experiment. The delayed luminescence is the longlived luminescence that is observed after suppression of all short-lived emissions with a mechanical chopper. The phosphorescence from BPT can be observed as prompt luminescence and as delayed luminescence.

Experimental

The basic experimental technique has been described in detail in a recent paper.¹⁸ Here we concentrate on experimental pecularities of the investigation of the luminescence from BPT.

4-H-1-Benzopyrane-4-thione

The precursor, chromone, was prepared in a two-step synthesis.¹⁹ Chromone was transformed into BPT by replacing the carbonyl oxygen atom in chromone by a sulfur atom with

[†] This is true also for the conceivable detection of S₁ by measuring the transient absorption S₁ \rightarrow S_n. Starting from a dominant primary population of S₁, the transient absorption would decay biexponentially; the fast component would yield the rate constant for intersystem crossing S₁ \rightarrow T₁ and the slow component would yield k_T^0 ; and not β_{S_1} .

Lawesson's reagant.²⁰ The raw product was purified in three steps: column chromatography on aluminium oxide with chloroform as solvent, recrystallization from light petroleum, and HPLC on Nucleosil 7 OH with a mixture of 97.5% isooctane and 2.5% of chloroform. The final product was stored in the dark under a nitrogen atmosphere in a freezer.

Perfluoro-1,3-dimethylcyclohexane

Commercial technical PF-1,3-DMCH contains a high percentage of other perfluorohydrocarbons as impurities. Essentially pure PF-1,3-DMCH was obtained by rectification over a 1 m distillation column with a high reflux ratio. The lowerboiling impurity was perfluoromethylcyclohexane (boiling point 76.3 °C). The higher-boiling impurities were not identified. Traces of water and of residual impurities in PF-1,3-DMCH were removed immediately before use by chromatography with aluminium oxide under a nitrogen atmosphere.

Samples

The main experimental problem in a quantitative investigation of the photophysical properties of thiones comes from their photochemical instability. This problem can be greatly reduced by using a special glass apparatus with a fluorescence flow cell, which is part of a closed circuit containing ca. 200 ml of a solution. Only a very small portion of the solution (ca. 0.01 ml) is irradiated by excitation light, and photoproducts are diluted over the whole volume. The glass apparatus is essentially identical with that shown in Fig. 3 of ref. 18. The only difference is an additional normal absorption cell with 1 cm pathlength, which is attached to the upper horizontal tube and allows one to measure the absorption spectrum of the enclosed solution.

Degassing of the solvent

In order to obtain the true unimolecular triplet decay rate constant $k_{\rm T}^0$ by extrapolation to infinite dilution, the quenching of T_1 by molecular oxygen should contribute less than 0.1% to the triplet decay. For a fluid solution and an inherently short-lived triplet state like that of BPT, this requirement should be satisfied if the concentration of dissolved oxygen is less than 10^{-8} mol dm⁻³. The solubility of oxygen in perfluoroalkanes is high;^{4,21} as a rule of thumb, the concentration of dissolved oxygen in a perfluoroalkane at room temperature is roughly equal to the oxygen concentration in the vapour phase, which corresponds to $ca. 0.01 \text{ mol } dm^{-3}$ for an air-saturated solvent. The removal of oxygen by the freezepump-thaw technique is not very efficient. We estimate that the reduction of the concentration of dissolved oxygen by a single freeze-pump-thaw cycle has been typically ca. 50%. It took about 15 freeze-pump-thaw cycles until at the beginning of a pump phase no rise of the residual gas pressure in the vacuum line was detectable. By applying a total of 30 freezepump-thaw cycles, samples with a reproducible triplet lifetime were obtained. Prior to use the samples were exposed to yellow room light only.

Concentration of BPT

For the determination of the rate constant k_Q for concentration quenching, the absolute concentration of BPT had to be known. At the higher concentrations ($\geq 9 \times 10^{-7} \text{ mol dm}^{-3}$), the concentration of BPT was calculated from the UV absorption spectrum of the sample. At the lower concentrations ($\leq 3 \times 10^{-7} \text{ mol dm}^{-3}$), which are important for extrapolating k_T to zero concentration, this procedure was not accurate enough. In this case, reliable relative concentrations can be determined by measuring the concentration-dependent intensity ratio of the prompt $S_2 \rightarrow S_0$ fluorescence of BPT and of a strong Raman band of the solvent.

Temperature

The glass apparatus with the fluorescence flow cell was connected to the external circuits of two rotary cryostats. The temperature of the solution was measured at the exit of the fluorescence flow cell with a calibrated thermocouple with an absolute accuracy of ± 0.5 K. The temperature was kept constant within ± 0.2 K.

Excitation

For all luminescence experiments, BPT was excited to S_2 with the 363.8 nm line of an argon ion laser (Spectra Physics model 2045–15). The power of the unchopped laser beam in the sample did not exceed 10 mW. The laser beam diameter was *ca.* 1 mm in the sample.

Chopper

An essential feature of the present investigation is the use of a fast mechanical chopper for suppressing disturbing prompt emissions (prompt fluorescence, Rayleigh- and Raman-scattered light). The chopper consists of two disks on a common shaft in an evacuated housing. Each disk has 40 segments and runs between a pair of slits of width w = 1 mm. The deadtime t_{dead} of the chopper is defined as the time passing from the beginning closure of the excitation slit to the full opening of the luminescence slit: $t_{dead} = (2w + s)/2\pi rf$, where s = 0.5 mm is the overlap width, r = 90 mm is the radius of a chopper disk in the centre of a slit, and $20 \leq f/Hz \leq 600$ is the rotation frequency of the chopper.

Monochromator

The home-built instrument is a double monochromator with two pairs of permanently installed holographic gratings with 3600 grooves mm^{-1} for the ultraviolet and visible regions up to 490 nm and with 1440 grooves mm^{-1} for the visible and the near-IR regions. It can be operated alternatively with additive or subtractive dispersion. Spectra were measured with additive dispersion. Decay curves of delayed luminescences were measured with subtractive dispersion, the maximum bandwidths being 12 and 30 nm. For measurements above 650 nm, the second-order UV transmission of the monochromator was blocked by a 10 mm absorption cuvette with a saturated aqueous solution of potassium bichromate.

Photomultiplier

The photomultiplier was a flat-end tube with S20 photocathode and extended red-sensitivity (EMI 9659 QA). The dark-count rate was reduced to *ca.* 2 Hz by cooling to -30 °C.

Electronics and data evaluation

The photon-counting technique was used. For measurement of the spectra of delayed luminescence, a synchronized electronic gate restricted photon-counting to the opening time of the luminescence slit of the chopper. Spectra and decay curves were accumulated in a Nicolet signal averager having a shortest channel dwell time of 1 μ s. All photon-counting data were corrected for dark-counts and, at high count rates, for pulse overlap. Luminescence spectra were corrected for the wavelength dependence of the sensitivity of the spectrometer.

Sequence of experiments

The triplet-decay rate constant $k_{\rm T}$ was the quantity to be determined most accurately. In order to minimize the effect of the photochemical degradation of a sample on the values of $k_{\rm T}$, the temperature dependence of $k_{\rm T}$ was measured first, starting with the lowest temperature.

735

The maximum absorption coefficient of BPT in the visible at 580 nm is ca. 13 dm³ mol⁻¹ cm⁻¹. By using a nearly saturated solution of BPT in PF-1,3-DMCH (ca. 2×10^{-4} mol dm⁻³) and an optical pathlength of 5 cm, a maximum absorbance of order ca. 0.013 is achieved. In order to measure this small absorbance with an accuracy of ca. 1%, a very good absorption spectrometer is needed. The absorption spectrum in Fig. 2 and 8 was measured with a Cary 5 spectrometer (Varian); a virtually identical spectrum was obtained with a Lambda 19 spectrometer (Perkin Elmer).

Results and Discussion

Temperature-dependent concentration quenching of the triplet state

The primary kinetic quantity to be determined is the firstorder rate constant k_T for the triplet decay of BPT. This is obtained from the monoexponential decay of the phosphorescence. A typical phosphorescence decay curve is depicted in Fig. 3. The phosphorescence decay was measured at six different concentrations of BPT in the temperature range between 230 and 300 K. Fig. 4 represents the measured values of k_T in a Stern–Volmer plot. At all temperatures the decay rate constant k_T is linearly dependent on the concentration c_0 of BPT:

$$k_{\rm T} = k_{\rm T}^0 + k_{\rm O} c_0 \tag{1}$$

 $(c_0$ is proportional to the density of the solvent; the resultant weak increase of c_0 with decreasing temperature was neglected.) For diffusion-controlled concentration quenching one expects k_0 to be proportional to the ratio T/η of tem-



Fig. 3 Decay curve of the phosphorescence from BPT $(1.6 \times 10^{-6} \text{ mol dm}^{-3})$ in PF-1,3-DMCH at 293 K. For the determination of the triplet lifetime the part of the curve between 40 and 70 µs can be used.



Fig. 4 Stern—Volmer plot of the concentration-dependent triplet decay rate constant k_{T} of BPT in PF-1,3-DMCH



Fig. 5 Dependence of the rate constant k_Q for concentrationquenching of T_1 of BPT in PF-1,3-DMCH on $T\eta^{-1}$ (η : viscosity). The intercept 0.0 was fixed.

perature T and viscosity η . The plot of k_Q vs. T/η in Fig. 5 confirms this expectation. The quantities of particular interest are the values of k_T^0 in Table 1, which were obtained by linear extrapolation of k_T to the BPT concentration $c_0 = 0$. The parameter values for 300 K agree with published room-temperature values: $k_Q = (6.9 \pm 0.6) \times 10^9 \text{ s}^{-1}$ and $1/k_T^0 = 16 \pm 2 \,\mu\text{s.}^8$

The complete spectrum of the prompt luminescence from BPT was also measured at all concentrations and temperatures. The ratio of the spectrally integrated intensities I_{PF_2} of the prompt $S_2 \rightarrow S_0$ fluorescence and I_P of the phosphorescence should be proportional to $k_{\rm T}$, if the quantum yields ϕ_{PF_2} of the prompt $S_2 \rightarrow S_0$ fluorescence and $\phi_{ISC}^{S_2}$ of intersystem crossing $S_2 \rightsquigarrow T_1$ (including intermediate internal conversion $S_2 \rightarrow S_1$ and the rate constant k_P for the radiative triplet decay are independent of temperature. In Fig. 6 the ratio $I_{\rm PF_2}/I_{\rm P}$ is plotted against $k_{\rm T}(T)$ for the highest BPT concentration. The relation $I_{\rm PF_2}/I_{\rm P} \propto k_{\rm T}$ is satisfied. With smaller concentrations of BPT, systematic positive deviations (up to ca. 10%) from the straight line in Fig. 6 were found, for which we have not yet a satisfactory explanation. The data in Fig. 6 can be compared with literature data as follows. The value of $I_{\rm PF_2}/I_{\rm P}$ at a given value of $k_{\rm T}$ should be equal to the literature value of the quantum yield ratio $\phi_{\rm PF_2}/\phi_{\rm P}$ referring to the same value of $k_{\rm T}$. With $\phi_{\rm PF_2} = 0.023 \pm 0.003^{1.14}$ and $\phi_{\rm P} = 0.076 \pm 0.008^{1.14,15}$ at $k_{\rm T}^{-1} = 16 \pm 2$ µs follows $\phi_{\rm PF_2}/\phi_{\rm P} \approx 0.30$; in excellent agreement with $I_{\rm PF_2}/I_{\rm P} \approx 0.30$ at $k_{\rm T} = 6.25 \times 10^4 \, {\rm s}^{-1}$ in Fig. 6 (note that the relative error of the ratio $\phi_{\rm PF}/\phi_{\rm P}$ should be considerably smaller than the relative errors of the absolute quantum yields $\phi_{\rm PF_2}$ and $\phi_{\rm P}$).

Table 1 Temperature dependence of the rate constants k_T^0 for unimolecular decay and k_Q for concentration quenching of the triplet state of BPT

	10-410	10-91		
T/K	$\frac{10^{-1} k_{\rm T}^2}{\rm /s^{-1}}$	$/dm^3 mol^{-1} cm^{-1}$	η/mPa s	$ ho/{ m g}~{ m cm}^{-3}$
300	5.89	6.5	1.93	1.851
293	5.62	5.4	2.24	1.868
290	5.50	4.9	2.40	1.875
280	5.12	3.8	3.05	1.899
270	4.78	2.8	3.98	1.923
260	4.46	2.0	5.34	1.947
250	4.15	1.5	7.43	1.972
240	3.88	0.9	10.8	1.996
230	3.64	0.5	16.8	2.020

The error limits are $\pm 0.3\%$ for $k_{\rm q}^{0}$ and $\pm 0.1 \times 10^{9}$ dm³ mol⁻¹ s⁻¹ for $k_{\rm q}$. The values of the viscosity η and the density ρ of the solvent PF-1,3-DMCH were calculated with eqn. (A1) and (A2) of the Appendix.



Fig. 6 Experimental verification of the proportionality $I_{PF_2}/I_P \propto k_T(T)$, where I_{PF_2} and I_P are the spectrally integrated intensities of the prompt $S_2 \rightarrow S_0$ fluorescence and the phosphorescence; the intercept 0.0 was fixed. The data refer to a BPT concentration of 5.4×10^{-6} mol dm⁻³.

Temperature dependence of unimolecular triplet decay

For the evaluation of the temperature dependence $k_0^{\alpha}(T)$ of the unimolecular triplet decay we have to make several simplifying assumptions.

(a) The state-specific decay rate constants β_{S_1} of S_1 and β_T^i of the three triplet substates $T_1^i(i = x, y, z)$ are assumed to be independent of temperature. (b) We neglect the possibility that vibrational fundamentals in vibronic S_1 states may significantly differ from those in vibronic T_1 states. (c) The two triplet substrates T_1^x and T_1^y can be treated as a single twofold degenerate state T_1^{xy} with an effective decay rate constant $\beta_T^{xy} = \frac{1}{2}(\beta_T^x + \beta_T^y)$. Since β_T^{xy} is much smaller than $\beta_{T,5}^z$ a fixed known value for β_T^{xy} can be used without much affecting the accuracy of the value of β_T^x . From $1/\beta_T^x = 1.1$ ms and $1/\beta_T^y = 1.8$ ms follows $\beta_T^{xy} \approx 730$ s⁻¹. (d) The energy difference $|D| = \Delta E(T_1^x, T_1^{xy})$ between T_1^{xy} and T_1^x is assumed to be independent of the solvent. We take the literature value $|D| \approx hc \times 20$ cm⁻¹.⁶

The unimolecular triplet decay rate constant k_T^0 can now be written as

$$k_{\rm T}^{\rm 0}({\rm T}) = p_{\rm T}^{xy}({\rm T})\beta_{\rm T}^{xy} + p_{\rm T}^{z}({\rm T})\beta_{\rm T}^{z} + p_{\rm S_1}({\rm T})\beta_{\rm S_1}$$
(2)

where the factors p(T) are temperature-dependent population probabilities for the respective excited states. Because of the very fast equilibration $T_1 \rightleftharpoons S_1$,¹⁰ the p(T) should be proportional to the respective Boltzmann factors. Thus the final expression for $k_T^0(T)$ is

$$k_{\rm T}^0 = C^{-1} [2\beta_{\rm T}^{xy} + \beta_{\rm T}^z \exp(-|D|/k_{\rm B}T) + \beta_{\rm S_1} \exp(-\Delta E({\rm S_1}, {\rm T_1^{xy}})/k_{\rm B}T)]$$
(3a)

where C is the sum of the Boltzmann factors,

$$C = 2 + \exp(-|D|/k_{\rm B}T) + \exp[-\Delta E(S_1, T_1^{\rm xy})/k_{\rm B}T]$$
 (3b)

In the temperature range of the experimental values (230– 300 K), the representation of the experimental values of k_T^0 by eqn. (3) does not sensitively depend on the particular value of |D|, as shown by the three curves in Fig. 7 and the parameter values in Table 2. Furthermore, a small systematic error in the measurement of the temperature of up to ± 0.5 K (cf. legend to Table 2) has only a small effect on the parameter values. In the following we refer to the parameter values calculated with $|D| = hc \times 20$ cm⁻¹.

For a comparison of the value of $\Delta E(S_1, T_1^{xy})$ with the 0,0 transitions $S_{0,0} \rightarrow S_{1,0}$ and $S_{0,0} \rightarrow T_{1,0}$ in the absorption spectrum, one has to take into account that the transition $S_0 \rightarrow T_1^x$ is much stronger than the transitions $S_0 \rightarrow T_1^x$ and $S_0 \rightarrow T_1^{y,0}$. Hence the energy difference $\Delta E(S_1, T_1)$ that is observable in the



Fig. 7 Temperature dependence of the unimolecular triplet decay rate constant k_T^0 . The three curves were obtained by fitting eqn. (3) to the experimental values of k_T^0 in Table 1 with constant $\beta_T^{xy} = 730$ cm⁻¹ and three different values of the zero-field splitting $|D| = E(T_1^x)$. $-E(T_1^{xy})$: (a) |D|/hc = 0 cm⁻¹ (---); (b) |D|/hc = 20 cm⁻¹ (----); (c) |D|/hc = 40 cm⁻¹ (---).

normal absorption spectrum should be equal to $\Delta E(S_1, T_1^x) = \Delta E(S_1, T_1^x) - |D|$. The kinetic value of $\Delta E(S_1, T_1^x)/hc$ (757 ± 13 cm⁻¹, see Table 2) is in excellent agreement with the spectroscopic value (750 ± 30 cm⁻¹).

The present determination of β_{S_1} from the temperature dependence of k_1^{T} of an aromatic thione seems to be the first such determination.¹ The value of β_{S_1} (4 × 10⁶ s⁻¹) is rather small. Nevertheless non-radiative internal conversion $S_1 \rightarrow S_0$ is the dominant decay process of S_1 . This follows from the fact that the $S_0 \rightarrow S_1$ transition is about as weak as the $S_0 \rightarrow T_1$ transition. Hence the rate constant for the radiative decays of S_1 (k_{F_1}) and T_1 (k_P) must be approximately equal: $k_{F_1} \approx k_P \approx 10^4 \text{ s}^{-1}$.¹ $\beta_{S_1} \approx 4 \times 10^{-6} \text{ s}^{-1}$ for BPT is smaller than $\beta_{S_1} \approx 2 \times 10^7 \text{ s}^{-1}$ estimated for xanthione.¹¹ Since S_1 of xanthione is ca. 1000 cm⁻¹ below S_1 of BPT, the rate of internal conversion $S_1 \rightarrow S_0$ in xanthione should be a factor of ca. 2 faster than in BPT (cf. Fig. 12 in ref. 1). Thus the present determination of β_{S_1} can be regarded as rough confirmation of the estimate of β_{S_1} for xanthione.

The value of $\beta_T^z(8.2 \times 10^4 \text{ s}^{-1})$ is by a factor of 1.3 greater than the literature value $(6.2 \times 10^4 \text{ s}^{-1.6})$. A much better agreement cannot be expected since on the one hand the lowtemperature value of β_T^z refers to a different solvent (hexane) and on the other hand the assumed complete independence of β_{s_1} and β_T^i on temperature cannot be expected to hold exactly. Thus we regard the agreement of the two values of β_T^z as satisfactory and as support of the basic assumption that k_T^0 is the rate constant for the unimolecular triplet decay of BPT.

Table 2 Parameter values obtained from the temperature dependence of the unimolecular triplet decay with eqn. (3) and the fixed value $\beta_T^{xy} \approx 730 \text{ s}^{-1}$

g	(<i>D</i> / <i>hc</i>) /cm ⁻¹	$10^{-4} \beta_{\rm T}^{\rm z}/{\rm s}^{-1}$	$10^{-6} \beta_{s_1}/s^{-1}$	$\frac{\Delta E(\mathbf{S}_1, \mathbf{T}_1^z/hc)}{/cm^{-1}}$
0	0	7.36 ± 0.11	3.84 ± 0.19	754 ± 12
+1	20	8.19 ± 0.12	4.10 ± 0.21	761 ± 13
0	20	8.22 ± 0.11	4.02 ± 0.20	757 ± 13
-1	20	8.26 ± 0.11	3.94 ± 0.20	754 ± 13
0	40	9.24 ± 0.12	4.23 ± 0.23	763 ± 14

 $\Delta E(S_1,T_1^z)$ is equal to $\Delta E(S_1,T_1^{zy}) - |D|$. The parameter g accounts for a conceivable systematic error in the temperature that linearly depends on temperature: $T_{\text{true}} = T_{\text{meas}} + [g \times (300\text{K} - T_{\text{meas}})/140];$ $g = \pm 1$ corresponds to a systematic error of ± 0.5 K at 230 K. The best values are those with g = 0 and $|D|/hc = 20 \text{ cm}^{-1}$.

Finally we should like to emphasize a unique feature of the thiones by comparing them with azulene. Azulene has three triplet state properties in common with the thiones: A very small energy difference between T_1 and S_1 (ca. $hc \times 450$ cm^{-1 22}), a very short triplet lifetime even at low temperatures (ca. 50 µs), and a temperature-dependent unimolecular triplet decay due to thermally activated intersystem crossing $T_1 \rightarrow$ S_1 .^{18,22} In contrast to the thiones, however, the intersystem crossing $T_1 \rightsquigarrow S_1$ is virtually irreversible owing to the extremely rapid internal conversion $S_1 \rightsquigarrow S_0$. As a consequence, the activation energy E_a that describes the temperature dependence of the unimolecular triplet decay of azulene contains information not on the energy difference between T_1 and S_1 , but on the vibronic triplet states $T_{1,\nu}$, which contribute most to the intersystem crossing $T_{1,v} \rightsquigarrow S_1$. Thus with BPT and azulene we have neat examples of the opposite extremes of thermally activated intersystem crossing: complete reversibility (cf. also ref. 3) and complete irreversibility.

Distinction between $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ absorption bands

In connection with the observability of E-type delayed fluorescence it is necessary to know the $S_0 \rightarrow S_1$ absorption spectrum at least approximately. If the $S_0 \rightarrow T_1$ spectrum were known, the $S_0 \rightarrow S_1$ absorption spectrum could be obtained by subtracting the $S_0 \rightarrow T_1$ spectrum from the measured absorption spectrum between 450 and 660 nm (cf. Fig. 2). The approximate $S_0 \rightarrow T_1$ absorption spectrum can be estimated by making use of the mirror image relation between an $A^* \rightarrow A$ emission spectrum and the corresponding $A \rightarrow A^*$ absorption spectrum. According to Förster,²³ the approximate relation between a corrected emission spectrum $f_e(\tilde{v}_e)$ and the absorption spectrum $\varepsilon_a(\tilde{v}_a)$ is

$$\tilde{v}_{e}^{-3} f_{e}(\tilde{v}_{e}) = \text{const.} \ \tilde{v}_{a}^{-1} \varepsilon_{a}(\tilde{v}_{a})$$
(4a)

$$\tilde{v}_{a} - \tilde{v}_{0,0} = \tilde{v}_{0,0} - \tilde{v}_{e} \tag{4b}$$

 $\epsilon(\tilde{v})$

ε_{S0}→_{T1}(ν̃)

ε_{S0}→s₁(ṽ)

22

where $\tilde{\nu}_{0,0}$ is the wavenumber of the common 0,0 transition. In the application of eqn. (4) we neglect the fact that part of the delayed luminescence is E-type delayed fluorescence and not phosphorescence. Even at the highest temperature (300 K) the relative population of S₁ is small ($p_S/p_T^z \approx 0.03$), and the contribution of E-type delayed fluorescence to the total delayed luminescence is $\lesssim 3\%$.

In Fig. 8 the four spectra of interest are compared: The corrected phosphorescence spectrum $f_{\mathbb{P}}(\tilde{v})$, the measured absorption spectrum $\varepsilon(\tilde{v})$, the approximate $S_0 \to T_1$ absorption spectrum $\varepsilon_{S_0 \to T_1}(\tilde{v})$, and the resulting difference spectrum $\varepsilon_{S_0 \to S_1}(\tilde{v})$, which is assigned to the $S_0 \to S_1$ transition.

 $\tilde{v}_{0.0}$

 $f_{\rm P}(\tilde{v})$

14

12

10

8

6

4

2

0

13

14

15

e / dm³ cm⁻¹ mol⁻¹



17

 $\tilde{v} / 10^3 \, {\rm cm}^{-1}$

18

19

20 21

16

Two features of the difference spectrum are important. First, the assignment of the peak at 16 700 cm⁻¹ to the origin band of the $S_0 \rightarrow S_1$ spectrum is confirmed. Secondly, in the whole range of the calculated approximate $S_0 \rightarrow S_1$ spectrum, the contribution of the $S_0 \rightarrow T_1$ transition to the total absorption cannot be neglected. In other words, at least in a liquid solution of BPT with strong inhomogeneous broadening, a selective excitation to S_1 is not possible.

Hot phosphorescence bands and E-type delayed $S_1 \rightarrow S_0$ fluorescence

A clear distinction between E-type delayed fluorescence and hot phosphorescence bands is possible, if the thermally activated intersystem crossing $T_1 \rightarrow S_1$ is reversible and the following relation holds for the rate constants k_{F_1} and k_P for spontaneous emission of fluorescence and phosphorescence,

$$k_{\mathbf{F}_{1}}(\mathbf{S}_{1,0} \to \mathbf{S}_{0,0}) = f \left[3 \sum_{v} k_{\mathbf{P}}(\mathbf{T}_{1,v} \to \mathbf{S}_{0,0}) \right] \text{ with } f \ge 1$$
 (5)

where the summation runs over all vibronic triplet states $T_{1,v}$ in the range of the inhomogeneously broadened 0,0 transition $S_{0,0} \rightarrow S_{1,0}$ and the factor 3 accounts for the threefold degeneracy of the triplet state. The classic example of an E-type delayed fluorescence is eosin itself;¹⁷ with this compound *f* is of the order of $\gtrsim 10^8$ (*cf.* Table 35 in ref. 17) and, despite a rather large energy gap of *ca.* $hc \times 3800$ cm⁻¹ between T₁ and S₁ (*cf.* Table 33 in ref. 17), the identification of the delayed fluorescence is unambiguous. Even if the thermally activated intersystem crossing T₁ \rightarrow S₁ is virtually completely irreversible, as in the case of azulene with a very low quantum yield of prompt S₁ \rightarrow S₀ fluorescence, an E-type delayed fluorescence can be easily distinguished from hot phosphorescence bands,²² because *f* is very large (*ca.* 10⁸).

In the case of thiones in general and of BPT in particular, the condition (5) for observing an E-type delayed fluorescence is obviously not satisfied. As revealed by the spectra in Fig. 8, in the range of $S_{1,0}$ roughly half of the absorption has to be assigned to the $S_0 \rightarrow T_1$ transition, which corresponds to $f \approx 1$ in eqn. (5). Thus a clear distinction between hot phosphorescence bands and E-type delayed fluorescence is expected to be difficult.

In Fig. 9, the spectra of prompt and delayed luminescence are depicted for temperatures of 300 and 230 K. At each temperature both spectra coincide up to *ca*. 500 cm⁻¹ above $T_{1,0}$. At higher wavenumbers, the spectrum of the prompt luminescence lies significantly above the spectrum of the delayed luminescence, and the assignment of part of the prompt luminescence to hot phosphorescence bands or E-type delayed

Fig. 9 Spectra of prompt luminescence (---) and delayed luminescence (---) from BPT (5.4 × 10⁻⁶ mol dm⁻³) in PF-1,3-DMCH at 230 and 300 K



The comparison of the hot-band region of the phosphorescence with the absorption spectrum is difficult because of the steep drop in intensity. The comparison of the two spectra is greatly facilitated by choosing a different representation of the hot-band range. We neglect the fact that in the temperature range covered most of the BPT molecules are not in $S_{0,0}$ but in low vibrational states $S_{0,v}$. Then in the absorption spectrum the vibronic transitions $S_{0,0} \rightarrow T_{1,v}$ and $S_{0,0} \rightarrow S_{1,w}$ are observed. In a measurement of delayed luminescence, the same final states are thermally populated from $T_{1,0}$ with the relative probability

$$p(\tilde{\mathbf{v}}, T) = \exp[-hc(\tilde{\mathbf{v}} - \tilde{\mathbf{v}}_{0,0})/k_{\rm B}T]$$
(6)

If in the hot-band range, $f_{HB}(\tilde{v})$, of the delayed-luminescence spectrum the inverse transitions $T_{1,v} \rightarrow S_{0,0}$ and $S_{1,u} \rightarrow S_{0,0}$ dominate, then the function $f_{HB}^*(\tilde{v}) = f_{HB}(\tilde{v})/p(\tilde{v},T)$ should be similar to the absorption spectrum $\epsilon(\tilde{v})$:

$$f_{\mathrm{HB}}^{*}(\tilde{v}) = f_{\mathrm{HB}}(\tilde{v}) \exp[+hc(\tilde{v} - \tilde{v}_{0,0})/k_{\mathrm{B}}T]$$
(7)

The spectral transformation (7) can be called an inverse Boltzmann weighting. Note that the spectral shape and the position of $f_{HB}^*(\tilde{v})$ are invariant against a change of $\tilde{v}_{0,0}$. In Fig. 10 the spectrum $f_{HB}^*(\tilde{v})$ for 300 K is compared with $e(\tilde{v})$ in a linear plot. The similarity between the two spectra is striking. $f_{HB}^*(\tilde{v})$ exhibits only a weak dependence on temperature, as illustrated by the four spectra in the logarithmic plot of Fig. 11.

The question, whether an E-type delayed fluorescence from BPT can be observed, has found a simple answer: At each wavenumber \tilde{v} , the relative contribution of E-type delayed fluorescence to the hot-band delayed luminescence is roughly equal to the relative contribution of the $S_0 \rightarrow S_1$ transition to the total absorption at \tilde{v} . Thus the second maximum of $f_{\text{HB}}^*(\tilde{v})$ at 16 700 cm⁻¹ is predominantly E-type delayed fluorescence, whereas the third maximum at 17 300 cm⁻¹ is predominantly hot-band phosphorescence.

The usual interpretation of hot luminescence as E-type delayed fluorescence is based in part on the determination of an activation energy E_a that is approximately equal to $\Delta E(S_1,T_1)^{24}$ From the approximate independence of $f_{\text{HB}}^*(\tilde{v})$ on temperature in Fig. 11 it immediately follows that E_a is an increasing linear function of \tilde{v} . The value of E_a alone is not

Fig. 10 Spectra of BPT in PF-1,3-DMCH at 300 K: (a) prompt (---) and delayed (---) luminescence; (b), (c) inverse Boltzmann-weighted representations $f_{HB}^{*}(\tilde{v})$ [*cf.* eqn. (7)] of the hot-band range of (b) the delayed luminescence (---) and (c) the prompt luminescence (---); (d) absorption spectrum $\varepsilon(\tilde{v})$ of BPT in relative units



Fig. 11 Logarithmic plot of the spectra (a), (b) and (c) of Fig. 10 at four temperatures and of the absorption spectrum (d) at room temperature

sufficient to distinguish an E-type delayed fluorescence from hot-band phosphorescence.

Conclusion

(i) From the temperature dependence of the unimolecular rate constant of triplet decay, k_T^0 , the values of three parameters can be calculated: the rate constants β_T and β_{S_1} for the individual decays of T_1 and S_1 to S_0 and the energy difference $\Delta E(S_1, T_1)$ between T_1 and S_1 .

(ii) The value of β_{S_1} is remarkably small (ca. $4 \times 10^6 \text{ s}^{-1}$). Nevertheless the dominant process in the decay of S_1 to S_0 is internal conversion $S_1 \rightsquigarrow S_0$.

(iii) In a refined treatment, the large zero-field splitting between the virtually degenerate doublet T_1^x, T_1^y and the higher substate T_1^z has to be taken into account. By relying on known values of the individual substate decay rate constants β_T^x and β_T^y and of the energy difference $E(T_{1z}^z) - E(T_1^{xy})$, the value of the decay rate constant β_T^z of T_1^z can be determined. The value of β_T^z (8.2 × 10⁴ s⁻¹) satisfactorily agrees with an indirectly determined low-temperature value.

(iv) The value of $\Delta E(S_1, T_1^z)$ ($hc \times 757 \text{ cm}^{-1}$) is in excellent agreement with the absorption contour bands that are assigned to the 0,0 transitions $S_{0,0} \rightarrow T_{1,0}$ and $S_{0,0} \rightarrow S_{1,0}$.

(v) The $S_0 \rightarrow S_1$ absorption spectrum can be obtained by subtracting the $S_0 \rightarrow T_1$ absorption spectrum from the total absorption spectrum of both transitions. The $S_0 \rightarrow T_1$ absorption spectrum can be approximately determined by assuming mirror symmetry between the $S_0 \rightarrow T_1$ absorption spectrum and the $T_1 \rightarrow S_0$ phosphorescence spectrum.

(vi) The hot-band range of the delayed luminescence relative to $T_{1,0}$ is easy to assign in an inverse Boltzmann-weighted representation {multiplication by $\exp[hc(\tilde{v} - \tilde{v}_{0,0})/k_BT]$ }. The first vibronic contour band in this representation consists predominantly of E-type delayed fluorescence.

(vii) For BPT in PF-1,3-DMCH, the known room temperature values of the rate constant k_Q for concentration quenching of T₁ and of the extrapolated rate constant k_T^0 of unimolecular triplet decay are confirmed.

(viii) $k_{\rm Q}$ is proportional to the ratio T/η of temperature T and viscosity η , as expected for diffusion-controlled concentration quenching.

B. N. thanks Prof. R. P. Steer for directing our interest to the photophysics of thiones, for providing a NATO Collaborative Research Grant (CRG 890941), and for comments to the present paper. H. E. gratefully acknowledges a graduate scholarship from the Fonds der Chemie. We thank Prof. J. Troe for generous support of this work, Dr. W. Kühnle for the synthesis and purification of BPT, H. Lesche for measuring



viscosity and density of PF-1,3-DMCH, and Dr. A. A. Ruth and Dr. M. T. Wick for comments to the manuscript. Finally we thank a referee for suggesting several improvements of the manuscript.

Appendix

Temperature dependence of viscosity and density of perfluoro-1,3-dimethylcyclohexane

The dynamic viscosity η and the density ρ of PF-1,3-DMCH were determined between 220 and 300 K with the methods described in ref. 26. $\eta(T)$ can be represented by the sum of two Arrhenius terms with an accuracy of $\pm 1\%$:

$$\eta(T) = B_1 \exp(E_1/RT) + B_2 \exp(E_2/RT)$$
 (A1)

The parameter values are: $B_1 = 5.163 \times 10^{-3}$ mPa s, $E_1/R = 1755.4$ K, $B_2 = 4.507 \times 10^{-7}$ mPa s, $E_2/R = 3777.7$ K.

The density ρ is with high accuracy a linear function of temperature in the studied temperature range:

$$\rho(T) = \rho_{25} + m(298.16 \text{ K} - T) \tag{A2}$$

with $\rho_{25} = 1.8552 \text{ g cm}^{-3}$, $m = 2.415 \times 10^{-3} \text{ g cm}^{-3} \text{ K}^{-1}$. The experimental values deviate from the fitted line (A2) by less than 0.1%. Since our value of ρ_{25} is larger than the literature value,^{1.27} $\rho_{25}^{\text{lit}} = 1.828 \text{ g cm}^{-3}$, we measured the density of 1,3-PF-DMCH also with a calibrated commercial pycnometer at 25 °C and obtained 1.854 g cm}-3}. This discrepancy may result from a less complete fluorination of the substance studied in ref. 27.

References

- 1 A. Maciejewski and R. P. Steer, Chem. Rev., 1993, 93, 67.
- 2 H. Eisenberger, B. Nickel, A. A. Ruth and R. P. Steer, J. Chem. Soc., Faraday Trans. 1996, 92, 741.

- 3 B. Nickel, H. Eisenberger, M. T. Wick and R. P. Steer, J. Chem. Soc., Faraday Trans, 1996, in the press.
- 4 A. Maciejewski, J. Photochem. Photobiol., A: Chem., 1990, 51, 87.
- 5 D. M. Burland, Chem. Phys. Lett., 1980, 70, 508.
- 6 M. J. Petrin, S. Ghosh and A. H. Maki, Chem. Phys., 1988, 120, 299.
- U. Brühlmann and J. R. Huber, Chem. Phys. Lett., 1978, 54, 606.
 J. Kozlowski, A. Maciejewski, M. Szymanski and R. P. Steer, J. Chem. Soc., Faraday Trans., 1992, 88, 557.
- 9 M. Szymanski, A. Maciejewski and R. P. Steer, Chem. Phys., 1988, 124, 143.
- 10 L. W. Molenkamp, D. P. Weitekamp and D. A. Wiersma, Chem. Phys. Lett., 1983, 99, 382.
- 11 A. Maciejewski, M. Szymanski and R. P. Steer, J. Phys. Chem., 1986, 90, 6314.
- 12 B. Nickel and G. Roden, Chem. Phys. Lett., 1980, 74, 368.
- 13 M. Mahaney and J. R. Huber, Chem. Phys., 1975, 9, 371.
- 14 A. Maciejewski, A. Safarzadeh-Amiri, R. E. Verrall and R. P. Steer, Chem. Phys., 1984, 87, 295.
- 15 M. Szymanski, A. Maciejewski and R. P. Steer, J. Phys. Chem., 1988, 92, 2485.
- 16 A. Maciejewski, M. Szymanski and R. P. Steer, J. Phys. Chem., 1988, 92, 6939.
- 17 C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.
- 18 B. Nickel and D. Klemp, Chem. Phys., 1993, 174, 297.
- 19 B. Föhlisch, Chem. Ber., 1971, 104, 348.
- 20 A. K. Baruah, D. Prajapati and J. S. Sanduh, *Tetrahedron*, 1988, 44, 6137.
- 21 B. Nickel and M. Flor Rodríguez Prieto, Ber. Bunsen-Ges. Phys. Chem., 1988, 92, 1493.
- 22 B. Nickel and D. Klemp, Chem. Phys., 1993, 174, 319.
- 23 Th. Förster, Fluoreszenz Organischer Verbindungen, Vandenhoeck & Ruprecht, Göttingen 1951, p. 142, eqn. (26,6').
- M. Szymanski and R. P. Steer, J. Phys. Chem., 1992, 96, 8719.
 J. B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970.
- 26 A. A. Ruth, B. Nickel and H. Lesche, Z. Phys. Chem., 1992, 175, 91.
- 27 R. N. Haszeldine and F. Smith, J. Chem. Soc., 1950, 2787.

Paper 5/04228C; Received 30th June 1995