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PHOTOCHEMISTRY AND PHOTOPHYSICS OF OSAZONES II: DIRECT AND SENSITIZED PHOTOISOMERIZATION OF D-"ARABINO"-HEXULOSE PHENYLOSAZONE

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Summary

The reversible direct and sensitized N-chelate → O-chelate (**A** → **B**) isomerization of D-"arabino"-hexulose phenylosazone (PH) was studied. The quantum yield of isomerization $\phi_{A \to B}$ was slightly influenced by the solvent properties but was not influenced by the concentration, the intensity of radiation or by external heavy atoms. With decreasing temperature $\phi_{A \to B}$ decreased significantly whereas the intensity of fluorescence of the **A** isomer increased.

On the basis of the quantum yields of intersystem crossing, of sensitization and quenching of **A** isomer fluorescence and of **A** → **B** photoisomerization, the reaction was shown to occur through the excited singlet states $^1A^*$ and $^1p^*$. $\phi_{A \to B}$ was limited by the efficiency of radiationless transitions to the perpendicular state $^1p^*$ in the $^1A^* \to {}^1p^*$ process and hence was relatively low. The low value of the rate constant of this process may result from the presence of the intramolecular N—H···N hydrogen bond and the quasi-aromatic ring in the **A** isomer. Photosensitized **A** → **B** isomerization was also found to take place following triplet–triplet energy transfer, with the reaction probably occurring through the $^3p^*$ state.

1. Introduction

Photoisomerization of organic compounds which occurs by twisting about a C=C double bond is one of the most extensively investigated photochemical reactions [1 - 3]. New experimental methods and theories have recently been employed to interpret the quantitative results of isomerization reactions of unsaturated aromatic hydrocarbons, particularly those of the stilbenes and their derivatives [1 - 7].

In contrast, photoisomerization about the C=N bond has been studied rather rarely, and quantitative results are available only for imines, oximes and hydrazones [8 - 10]. In a series of papers reporting the results of

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investigations of the *syn–anti* photoisomerization of phenylhydrazone derivatives produced by sensitization and quenching processes, Condorelli and coworkers [9, 11 - 13] have suggested that the direct reaction occurs via the excited singlet state. *Syn–anti* isomerization has also been reported to result from triplet–triplet energy transfer [11, 12]. N-chelate → O-chelate (A → B) photoisomerization (Section 3) of the osazones of sugar derivatives has been found to occur by twisting about one of the C=N bonds, and the photochromic properties of these compounds have been reported [14, 15]. The influence of the wavelength on the quantum yield of photoisomerization has also been examined.

In this paper we report quantitative data for the mechanism of the A → B photoisomerization (photomutarotation) of D-"arabino"-hexulose phenylosazone (D-glucose phenylosazone) (PH), the contribution of different excited states to the isomerization process and the influence of various factors, *e.g.* the intramolecular hydrogen bond, the sensitizers used and the temperature, on the mechanism of the reaction.

2. Experimental details

2.1. Direct N-chelate → O-chelate photoisomerization

The irradiation was performed using a high pressure HBO-200 mercury lamp (Narva) and an XBO-150 xenon lamp (Osram). Radiation of wavelength 366, 405 or 436 nm was selected using interference (Carl Zeiss) and absorption (Schott) filters or a double-prism M-3 monochromator (Cobrabid) with a half-peak width $\Delta\lambda$ of no more than 5 nm. The samples, with concentrations ranging from 10^{-6} to 10^{-3} M, were irradiated in cuvettes with a volume of 0.03 - 15 ml and a thickness of 0.005 - 5 cm. The concentrations and cuvette thicknesses were chosen so that the absorbance A_b would range from 0.3 to 1.0. The solutions studied were deoxygenated by purging with helium which had been passed through a column containing copper at a temperature T of 463 K and by 3A and 4A molecular sieves (Fluka). The oxygen concentration was determined by measuring the lifetime of triplet anthracene under these conditions using a laser flash photolysis apparatus [15] and was found to be 10^{-6} M or less. Photoisomerization was perfomred at 293 and 77 K; the lower temperature was achieved by placing the cuvette in a quartz Dewar containing liquid nitrogen. The progress of photoisomerization was monitored by measuring the UV and circular dichroism (CD) spectra using UV–VIS Specord (Carl Zeiss) and Cary 118C (Varian) spectrometers and a Dichrograph mark III (Jobin–Yvon) spectropolarimeter. The measurement procedure has been described in detail in ref. 15.

The photoisomerization reaction was shown to be the only one taking place in view of the observation of five isosbestic points in the UV spectrum and two isosbestic points in the CD spectrum and the fact that a distinct photostationary state was obtained in the system. The UV and CD spectra were used to calculate the quantum yields of A → B photoisomerization in

systems for which a maximum conversion of 15% was attainable. The values obtained were extrapolated to zero conversion. The photostationary state was attained after irradiation for 1 - 5 min. Longer exposures, from 30 to 100 min, caused the photodecomposition of PH which was also monitored by UV and CD spectra. The intensity of the absorbed radiation was determined using uranyl oxalate [16] and Reinecke's salt [17].

2.2. Sensitization and quenching of N-chelate → O-chelate photoisomerization

The irradiation was performed using the same apparatus as that described in Section 2.1 together with a low pressure TNN 15/32 lamp (Original Hanau) in order to obtain $\lambda = 254$ nm. Monochromatic radiation with wavelengths of 458 and 476.5 nm was obtained using ILA-120 (Carl Zeiss) and 52 G (Coherent Radiation) argon ion lasers. The power of the incident light and of the light transmitted through the sample was measured using a KB-6301 power meter (Cobrabid). The power meter was calibrated with an accuracy to ±5% by an absolute method using Reinecke's salt as a chemical actinometer [18].

The concentrations of sensitizers, quenchers and the osazone A ranged from 10^{-3} to 10^{-5} M, 10^{-2} to 10^{-5} M and 10^{-2} to 10^{-5} M respectively. These concentrations were chosen so that A would absorb no more than 1% of the radiation in the sensitized reaction (except for perylene when A absorbed about 10% of the radiation) and at least 95% of the radiation in the quenching reaction. All samples were carefully deoxygenated, except when studying the influence of oxygen.

In order to check whether ground or excited state complexes between PH and the sensitizers (quenchers) existed, the UV, CD and fluorescence spectra were measured. To ensure that the A → B photoisomerization reaction in the sensitizer–PH system occurred only as a result of energy transfer, comparative measurements were always performed for samples containing PH only. The sensitized B → A photoisomerization was not studied because the rate of thermal isomerization was too fast to obtain accurate results.

2.3. Fluorescence

Corrected and uncorrected fluorescence spectra of A [19] in both the presence and the absence of quenchers and the fluorescence spectra of the sensitizers in both the presence and the absence of A were measured using MPF-3 (Perkin–Elmer–Hitachi) and MPF-44 (Perkin–Elmer) spectrofluorometers. Deoxygenated solutions were studied at the same concentrations and using the same excitation wavelengths as in the photoisomerization reaction. The effect of the quenchers was to decrease the fluorescence intensity of the A isomer; there was no change in the shape of the fluorescence spectrum. This result implies that fluorescence quenching occurs by intermolecular energy transfer. The decrease in the intensity of the tetracene fluorescence in the presence of A occurred in a similar manner. One exception involved the reabsorption of anthracene fluorescence by A, and this behaviour was taken into account in the calculations.

2.4. Laser flash photolysis

The kinetics of the excited states were studied using a modified nanosecond laser photolysis system [20]. Excitation was carried out using the second harmonic (potassium dihydrogen phosphate) of a ruby laser at a wavelength of 347 nm. The pulse width was 12 - 15 ns, the peak power was 1×10^5 - 3×10^6 W and the power density was 1×10^7 - 3×10^8 W cm^{-2}. The laser radiation was focused on the surface of a cuvette of dimensions 1 cm × 0.1 cm which contained the sample. The transient absorption was monitored using a pulsed xenon lamp (IM-500 W), with a pulse time t of 1 - 10 ms. The analysing beam was made parallel by a lens and diaphragms and, after passing through the filters, it was incident on the first millimetre of the laser-irradiated sample perpendicular to the laser radiation. The analysing beam was then passed through a double-prism M-3 monochromator (Cobrabid) of high brightness and was recorded using 1P-28 (RCA) or R-446 and R-928 (Hamamatsu) photomultipliers. The absorption signal was registered using either a 150 MHz or a 250 MHz oscilloscope and was photographed. The energies of the incident radiation and of the radiation passing through the sample were measured using 1P-28 photomultipliers and EZ-10 recorders (CSSR) which had been calibrated by an actinometric method [18].

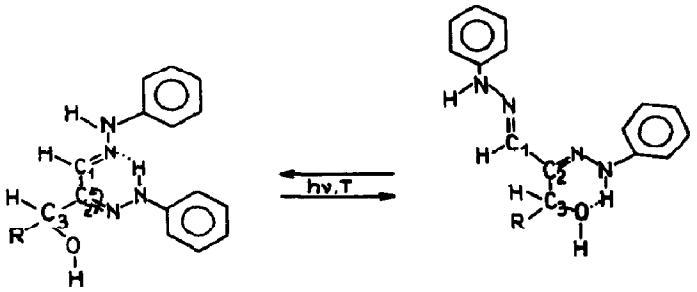
2.5. Materials

The N-chelate and O-chelate isomers of PH were synthesized and purified as described in ref. 15. The O-chelate isomer was synthesized photochemically with an efficiency of more than 95% by using an argon laser (λ = 458 nm). The solvents used in the direct isomerization reaction were fluorescence grade 95% ethyl alcohol (EtOH) (Merck), absolute EtOH, spectroscopic grade glycerine and dioxane (Merck and Fluka) and ethylene glycol puriss (Fluka). The solvents were used as received except that water was removed using 3A and 4A molecular sieves. Because of the low solubility of tetracene and A in EtOH the solvent used in the tetracene-sensitized isomerization reaction was spectroscopic grade dimethyl sulphoxide (DMSO) (Merck) which was purified by fractional distillation under reduced pressure in the presence of helium. Ethyl iodide (puriss, POCh) was also used as a solvent and was purified by fractional distillation under reduced pressure. The following compounds were used as sensitizers and quenchers: benzophenone (puriss, Aldrich, Fluka), anthracene (puriss, Kodak, Fluka), azulene (puriss, Fluka), and tetracene and perylene (Aldrich). All these compounds were additionally purified by triple crystallization from EtOH, benzene or toluene. Anthracene was also purified by sublimation. *n*-butyl mercaptan (puriss, Fluka) with no additional purification was used as a free-radical scavenger.

3. Results

3.1. Direct isomerization N-chelate → O-chelate (A → B)

The reversible process of A → B photoisomerization occurs according to the reaction [14, 15, 21]



A N-chelate

B O-chelate

where R ≡ $(HCOH)_2CH_2OH$.

In this paper we study the influence of solvent properties on the mechanism and quantum yield of A → B photoisomerization. Regardless of the solvent used, the same A → B reaction as reported for the thermal isomerization [21] was found to occur. This conclusion follows from the fact that both the isosbestic points in the UV and CD spectra and the linear extinction difference (ED) diagrams [22] were the same for thermal isomerization and photoisomerization. The solvents used differed in polarity, viscosity, hydrogen donating ability and basicity. On irradiating the A isomer ($c = 5 \times 10^{-5}$ M) at 436 nm and a temperature of 293 ± 1 K, the solvent properties were found to have a slight effect on $\phi_{A \to B}$ (Table 1).

Changes in the concentration of the A isomer in the range 10^{-3} - 10^{-6} M did not affect either the $\phi_{A \to B}$ value or the position $([A]/[B])_s$ of the photostationary state for photoisomerization in 95% EtOH at λ = 436 nm (unless indicated otherwise 95% EtOH was used as the solvent). Changes in the incident light intensity I_0 in the range 1×10^{15} - 1×10^{17} quanta s^{-1} cm^{-3} for λ = 366 nm also had no effect on either $\phi_{A \to B}$ or $([A]/[B])_s$ for PH at concentrations in the range 10^{-4} - 10^{-5} M.

TABLE 1

Quantum yields $\phi_{A \to B}$ of direct A → B isomerization in various solvents

Solvent	$\phi_{A \to B}$ [a]	*Dielectric constant* ϵ	*Dipole moment* μ (debye)	*Viscosity* η (cP)	p*K* [b]
EtOH (95%)	0.031 ± 0.004	—	—	—	—
EtOH (100%)	0.030 ± 0.005	24.3	1.7	10.8	−2.4
Dioxan	0.025 ± 0.004	2.2	0	10.9	−4.4
Ethylene glycol	0.027 ± 0.004	37.7	2.3	136	0
Glycerine	0.025 ± 0.005	42.5	2.6	9450	—

[a] Each value reported is the arithmetic mean of the results of at least three measurements, and the error given is the root mean square of the average.
[b] p*K* ([base]/[H_2O]) is the basic constant.

However, $\phi_{A \to B}$ for PH irradiated at λ = 436 nm was found to be significantly affected by temperature. At 77 K its value was 1×10^{-3}, which was a factor of 30 lower than its value at 293 K [15]. The intensity F_A of fluorescence of the A isomer was found to increase appreciably with decreasing temperature.

The addition of an effective free-radical scavenger such as *n*-butyl mercaptan [23] at a concentration of 0.02 - 1 M in 95% EtOH proved to have no effect on $\phi_{A \to B}$ for PH irradiated at λ = 436 nm. Using C_2H_5I as a heavy atom solvent instead of 95% EtOH also had no effect on $\phi_{A \to B}$.

3.2. Quenching of N-chelate → O-chelate isomerization and N-chelate fluorescence

In order to obtain information about the direct photoisomerization mechanism, A isomer fluorescence and A → B isomerization quenching were studied. The quenchers used were oxygen and azulene. Consideration of the energies of the lowest excited singlet (S_1) and triplet (T_1) states of the quenchers shows that both the T_1 and S_1 states of the A isomer of PH could be quenched. At a quencher concentration of 2×10^{-4} M, neither A → B isomerization nor fluorescence of the A isomer were quenched. At concentrations greater than 1×10^{-3} M quenchers have the same effect on both $\phi_{A \to B}$ and F_A (Table 2).

Identical linear dependences of $\phi_{A \to B}^0/\phi_{A \to B}$ and F_A^0/F_A on oxygen concentration suggest that the quenching of both A → B isomerization and A fluorescence is caused only by singlet–singlet energy transfer in the process $^1A^* + {}^1Q \to {}^1A + {}^1Q^*$ and that no chemical reaction occurs between A and Q. The results obtained are described well by the Stern–Volmer equation

$$\frac{\phi_{A \to B}^0}{\phi_{A \to B}} = \frac{F_A^0}{F_A} = 1 + k_q[Q]\tau_{^1A^*} \quad (1)$$

TABLE 2

The influence of oxygen concentration on the quantum yield $\phi_{A \to B}$ of A → B photoisomerization and the intensity F_A of fluorescence of the A isomer

Oxygen concentration (M)	$\phi_{A \to B}$ [a]	F_A [b]
$< 10^6$ [c]	0.031 ± 0.003	1.00 ± 0.06
1.9×10^{-3} [d]	0.029 ± 0.003	0.94 ± 0.05
8.9×10^{-3} [e]	0.024 ± 0.004	0.79 ± 0.06

The concentration of isomer A is 5×10^{-5} M in 95% EtOH; T = 293 K.
[a] Irradiation wavelength, 436 nm.
[b] The fluorescence is given in relative units; the excitation wavelengths are 350 and 390 nm.
[c] Oxygen concentration in the solution deoxygenated by purging with helium [15].
[d] Oxygen concentration in an air-saturated solution of 95% EtOH [24].
[e] Oxygen concentration in an oxygen-saturated solution of 95% EtOH [24].

where $\phi_{A \to B}{}^0$ and $\phi_{A \to B}$ are the quantum yields of A → B photoisomerization in the absence and the presence of oxygen respectively, $F_A{}^0$ and F_A are the intensities of A isomer fluorescence in the absence and the presence of oxygen, $\tau_{{}^1A^*}$ is the lifetime of the A isomer in the excited singlet state $^1A^*$ and k_q is the rate constant of quenching of the excited A isomer by oxygen.

The quenching of both A → B isomerization and A fluorescence gives the same value for the excited state lifetime ($\tau_{{}^1A^*} = 4.5 \times 10^{-9}$ s) and the same quenching constant ($K = k_q \tau_{{}^1A^*}$), equal to 30 M^{-1}, provided that $k_q = k_{diff}$ where k_{diff} is the diffusion-controlled rate constant of energy transfer. A similar value of $K = 20$ M^{-1} was obtained for both A → B isomerization and A fluorescence when azulene was used as a quencher ($c = (1 - 25) \times 10^{-3}$ M).

3.3. *Laser flash photolysis*

In order to confirm that the photoisomerization reaction proceeds via the excited singlet state $^1A^*$, the quantum yields $\phi_{S,T}$ of triplet state formation (intersystem crossing) were measured for the A isomer. A was used in concentrations of 3×10^{-4} - 3×10^{-5} M in deoxygenated 95% EtOH and the excitation was performed using laser radiation with $\lambda = 347$ nm and $t = 12$ ns. Two independent methods were used to measure $\phi_{S,T}$: a relative method described for the first time by Richards and Thomas [25] and developed by Bensasson and coworkers [26], and an absolute method described by Porter and Topp [27] and Soep *et al.* [28].

In the relative method anthracene and benzophenone were used as standard compounds. Anthracene at a concentration of 2×10^{-4} M in deoxygenated 95% EtOH was irradiated under the same conditions as A. $\phi_{S,T}$ for anthracene is 0.71 [24, 29] and the molar absorption coefficient ϵ_T of the $T_1 \to T_n$ transition is 64 700 M^{-1} cm^{-1} for $\lambda = 421$ nm [30]. Benzophenone at a concentration of 3×10^{-3} M in deoxygenated 95% EtOH, for which $\phi_{S,T} = 1$ [24, 31] and $\epsilon_T = 1100$ M^{-1} cm^{-1} at $\lambda = 640$ nm [32], was also used. The value of ϵ_T for A measured by the triplet–triplet energy transfer method [33] was 61 200 M^{-1} cm^{-1} at $\lambda = 460$ nm [19]. $\phi_{S,T}$ for isomer A was calculated from [26]

$$\phi_{S,T}{}^A = \phi_{S,T}{}^W \frac{OD^A}{OD^W} \frac{\epsilon_T{}^W}{\epsilon_T{}^A} \frac{I_a{}^W}{I_a{}^A} \frac{I_0{}^W}{I_0{}^A} \tag{2}$$

where W and A denote the standard and the A isomer respectively, OD denotes the optical density value for the transition $T_1 \to T_n$, I_a is the absorption at the excitation wavelength (in per cent) and I_0 is the intensity of the incident laser radiation at 347 nm. When, for both the standards and A, the intensity I_0 of the laser radiation is 1×10^{15} quanta $pulse^{-1}$ or less, the power density P is 3×10^{16} quanta cm^{-2} or less and OD is 0.1 or less [26], a value of $(6 \pm 2) \times 10^{-3}$ is obtained for $\phi_{S,T}{}^A$.

In the absolute method $\phi_{S,T}$ was calculated from [27, 28]

$$\phi_{S,T} = \frac{c_{T_1}}{I_{abs}} \tag{3}$$

where I_{abs} is the intensity of the absorbed laser radiation at the excitation wavelength. The concentration c_{T_1} of A in the T_1 state was calculated from

$$c_{T_1} = \frac{OD}{\epsilon_T l} \tag{4}$$

where l is the path length of the solution irradiated by the analysing xenon lamp. A value of $(5 \pm 2) \times 10^{-3}$ was obtained for $\phi_{S,T}$ which is consistent with the value obtained using the relative method within the limits of error.

Since low radiation intensities and laser power densities were used, effects such as non-linear optical phenomena [34], photoquenching [35] and thermal blooming of the beam [34] were not present in the irradiated system.

The singlet pathway for direct A → B photoisomerization of PH was independently confirmed by studying the quenching of the $T_1 \rightarrow T_n$ absorption of A ($c = 1 \times 10^{-4}$ M) [19] at wavelengths between 450 and 490 nm by azulene ($c = 5 \times 10^{-3}$ M) (Fig. 1). Under these conditions, azulene was found to quench the $T_1 \rightarrow T_n$ absorption signal of A completely. However, it only slightly (±15%) affected $\phi_{A \rightarrow B}$ and F_A (Section 3.2).

The measured lifetime of A ($c = 4 \times 10^{-4}$ - 4×10^{-5} M) in the T_1 state in deoxygenated 95% EtOH was $\tau_{T_1}{}^0 = 4.5 \times 10^{-7}$ s (Fig. 1), while in the presence of oxygen at a concentration of 1.89×10^{-3} M, $\tau_{T_1} = 2.5 \times 10^{-7}$ s. Thus the rate constant k_q of the energy transfer calculated from

$$\frac{1}{\tau_{T_1}} = \frac{1}{\tau_{T_1}{}^0} + k_q[Q] \tag{5}$$

was 1×10^9 M^{-1} s^{-1} while the quenching constant K was 450 M^{-1}.

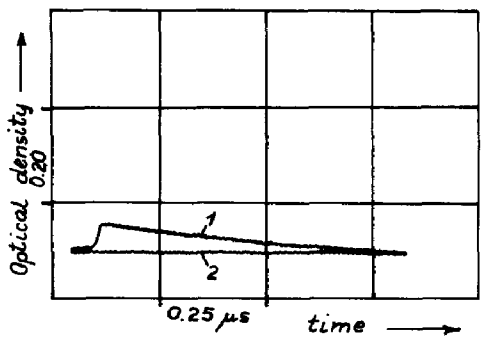


Fig. 1. Oscilloscope traces for the decay of the triplet intermediate in laser flash photolysis: transient absorption ($T_1 \rightarrow T_n$) signals of isomer A of PH ($c = 1 \times 10^{-4}$ M) in the absence (curve 1) and in the presence (curve 2) of azulene ($c = 5 \times 10^{-3}$ M) in deoxygenated 95% EtOH (T = 293 K; λ = 450 nm).

3.4. Sensitized N-chelate → O-chelate photoisomerization of D-"arabino"-hexulose phenylosazone

3.4.1. Singlet → singlet sensitization

Studies were undertaken to find the cause of the small value of $\phi_{A \rightarrow B}$ in direct photoisomerization [15]. The results of the laser flash photolysis

experiments (Section 3.3) imply that direct A → B photoisomerization occurs via the excited singlet state. Our object was to establish the mechanism of isomerization, and in particular to determine whether the spectroscopically unobservable twisted state $^1p^*$ was involved in the photoisomerization and, if so, to determine the efficiency of its formation. Thus the sensitized isomerization experiments described below were performed.

Tetracene at a concentration of 4.6×10^{-4} M in DMSO was used as the sensitizer for the A → B photoisomerization of PH ($c = 10^{-5}$ - 10^{-2} M). Radiation of wavelength 476.5 mm from an argon laser was absorbed only by tetracene. This compound was chosen on the basis of the energies of its excited S_1 and T_1 states ($E_{S_1} = 60$ kcal mol^{-1} [24, 36] and $E_{T_1} = 30$ kcal mol^{-1} [24, 37] in polar solvents). The energies of the excited states of A in 95% EtOH are $E_{S_1} = 65 \pm 2$ kcal mol^{-1} [19] and $E_{T_1} = 40 \pm 2$ kcal mol^{-1} [19]. Thus a sensitized A → B isomerization due to the T_1(tetracene) → T_1(A) energy transfer is impossible.

In the present experiment the energies of the S_1 states of tetracene and A in DMSO were calculated independently of the UV, CD and fluorescence spectra to be $E_{S_1} = 58$ kcal mol^{-1} and $E_{S_1} = 63$ kcal mol^{-1} respectively. Thus energy transfer between S_1(tetracene) and S_1(A) can be excluded because the S_1(tetracene) lifetime τ_{S_1} in both polar and non-polar solvents is 6×10^{-9} s [24] and because $\Delta E = E_{S_1}(\text{tetracene}) - E_{S_1}(\text{A})$ is -5 kcal mol^{-1}. Thus the rate constant for energy transfer should be approximately 8×10^5 M^{-1} s^{-1} according to the relation given by Sandros [38].

It has also been shown that energy transfer does not occur from T_1(tetracene) ($\phi_{S,T} = 0.63$ in benzene [39]) to the twisted triplet $^3p^*$ [1 - 3, 40] of PH with $E_{^3p^*} = 33$ kcal mol^{-1} [19] because a sensitized A → B isomerization has not been observed despite the facts that τ_{T_1} was greater than 10^{-5} s for tetracene [30, 39] and that the concentration of A was in the range $(1 - 10) \times 10^{-4}$ M.

However, when solutions of A with concentrations in the range 4×10^{-3} - 1.5×10^{-2} M were used, A → B isomerization sensitized by tetracene was found to occur. The corresponding changes in the UV (Fig. 2) and CD spectra, the numbers of isosbestic points and the linear ED diagrams [22] obtained at an arbitrary wavelength were the same as in the case of direct isomerization in 95% EtOH. The absorption maxima were shifted bathochromically by about 500 cm^{-1} owing to the influence of the solvent polarity on π,π^* transitions.

The concentrations of A were chosen in such a way that the competing absorption by osazone and the formation of ground state complexes with tetracene would not occur. Under such conditions energy transfer from tetracene to A occurred with an efficiency of 10% - 50% depending on the concentration of A. On irradiation the tetracene gradually disappeared owing to photolysis; this process was carefully measured and taken into account in the calculations of the intensity of the absorbed radiation. The apparent quantum yield $\phi_{A \to B}^{app}$ of sensitized A → B photoisomerization was found to increase with the concentration of A. The plot of $1/\phi_{A \to B}^{app}$ *versus* 1/[A],

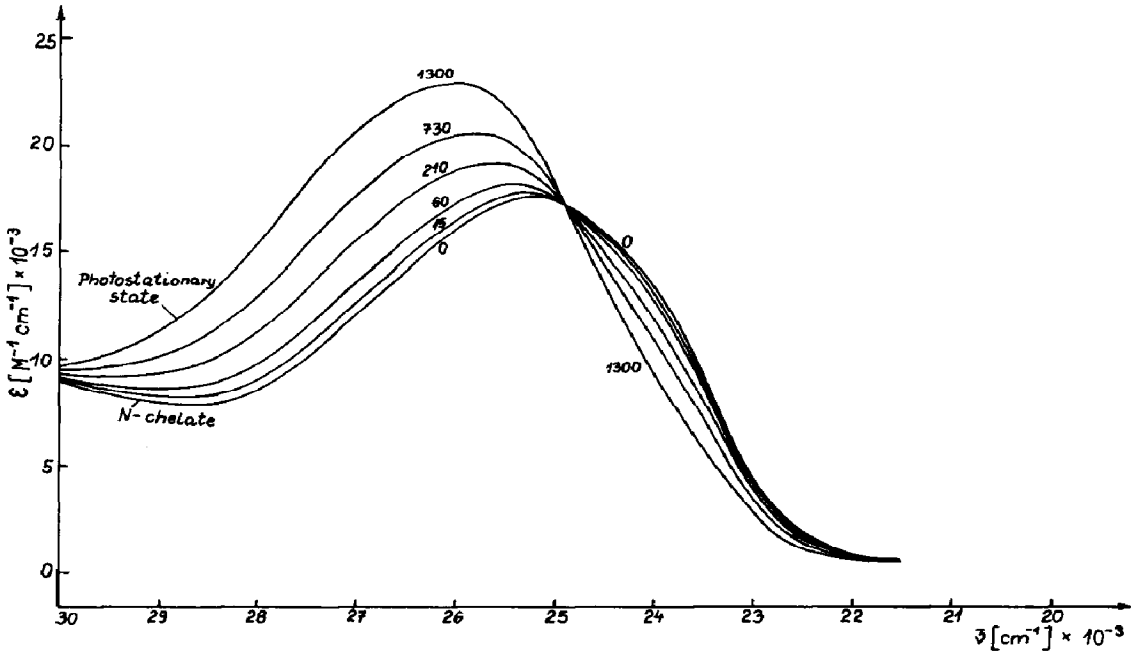


Fig. 2. Spectral changes in the UV spectra after the N-chelate → O-chelate (A → B) photoisomerization of PH ($c = 6.9 \times 10^{-3}$ M) sensitized with tetracene ($c = 4.6 \times 10^{-4}$ M) in DMSO by irradiation at $\lambda = 476.5$ nm and $T = 293$ K. The numbers on the curves give the irradiation time in seconds.

following the usual reaction scheme [41], gives a good straight line (Fig. 3(a)). The value of the limiting quantum yield of $\phi_{A \to B}^{sens}$ was obtained by extrapolation to $1/[A] \to 0$, *i.e.* to the conditions when the acceptor captured all the sensitizer singlets [41]. The value obtained was $\phi_{A \to B}^{sens} = 0.48 \pm 0.08$ while $([A]/[B])_s = 1.1 \pm 0.2$. When these values were used and the relation [1 - 3]

$$\frac{\phi_{A \to B}^{sens}}{\phi_{B \to A}^{sens}} = \left(\frac{[B]}{[A]}\right)_s^{sens} \tag{6}$$

was applied a value of $\phi_{B \to A}^{sens}$ was obtained. The ratio of the intercept to the slope gives a value of 30 M^{-1} for the sensitization constant K. If it is assumed that $\tau_{S_1} = 6 \times 10^{-9}$ s for tetracene in DMSO [24], the rate constant of energy transfer k_q is $(5 \pm 2) \times 10^9$ M^{-1} s^{-1}, *i.e.* the process is almost diffusion controlled.

The results obtained suggest that the sensitized isomerization A → B occurs by energy transfer from ^{1}S(tetracene) to ^{1}p*(PH). In order to confirm this suggestion we showed that, under the same conditions as those for the sensitized A → B isomerization, the tetracene fluorescence was quenched by A while the ratio of the intensity F_t^0 of the tetracene fluorescence in the absence of A to the intensity F_t in the presence of A changed linearly with the concentration of A within the range $(4 - 15) \times 10^{-3}$ M (Fig. 3(b)).

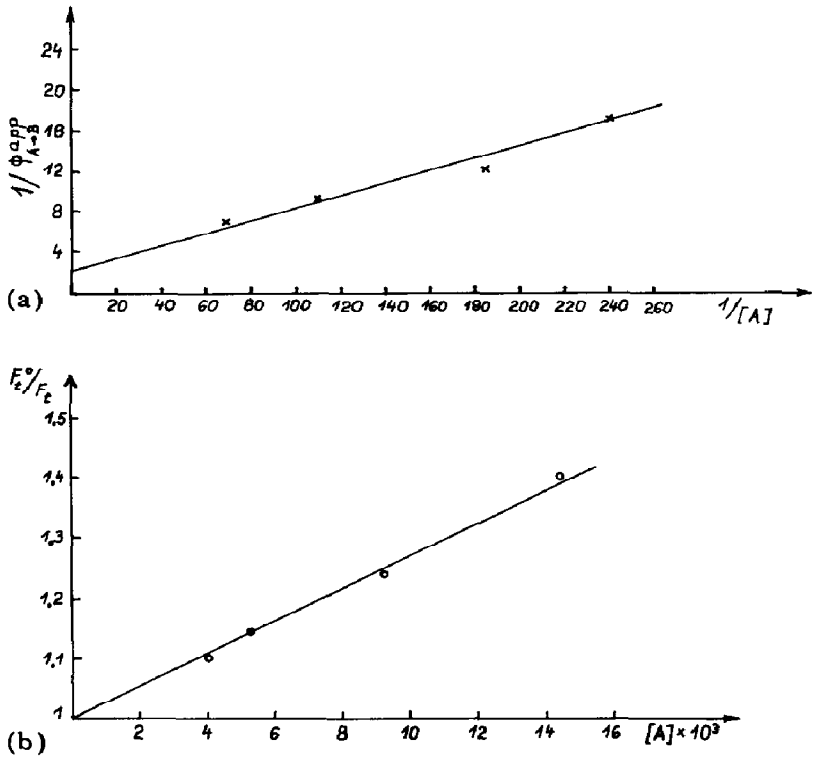


Fig. 3. (a) The N-chelate → O-chelate (A → B) isomerization of PH photosensitized by tetracene; (b) the Stern–Volmer plot for the quenching of tetracene fluorescence by the N-chelate (A) isomer of PH.

The rate constant of energy transfer k_q was $(5 \pm 1) \times 10^9$ M^{-1} s^{-1} (from eqn. (1)), assuming that for tetracene in DMSO $\tau_{S_1} = 6 \times 10^{-9}$ s [24]. This is consistent with the value of k_q obtained in the sensitized photoisomerization. Neither sensitized fluorescence of A nor any other emission was found. In contrast, under the conditions employed in this experiment the quantum yield ϕ_A of the tetracene-sensitized photolysis of A obtained from UV and CD spectra was less than 1.7×10^{-4}. Thus the contribution of this process can be neglected in investigations of sensitized A → B isomerization.

3.4.2. Triplet–triplet sensitization

Since the quantum yield $\phi_{S,T}$ of T_1 state formation for isomer A is 6×10^{-3} (Section 3.3), the singlet state $^1A^*$ is involved in direct A → B photoisomerization. In order to determine whether isomerization can also occur in the triplet states and, if so, to find its mechanism and quantum yield, the sensitized A → B isomerization due to the triplet–triplet energy transfer was studied. Anthracene, perylene in 95% EtOH and tetracene in DMSO (Section 3.4.1) were used as sensitizers. For anthracene in EtOH $E_{T_1} = 42.5$ kcal mol^{-1} [24], $E_{S_1} = 76.3$ kcal mol^{-1} [24], $\phi_{S,T} = 0.71$ [24, 26, 29] and $\tau_{S_1} = 6 \times 10^{-9}$ s [24, 42]. The lifetime of the T_1 state of anthracene ($c = 3 \times 10^{-3}$ M) in deoxygenated 95% EtOH measured in the laser flash photolysis system

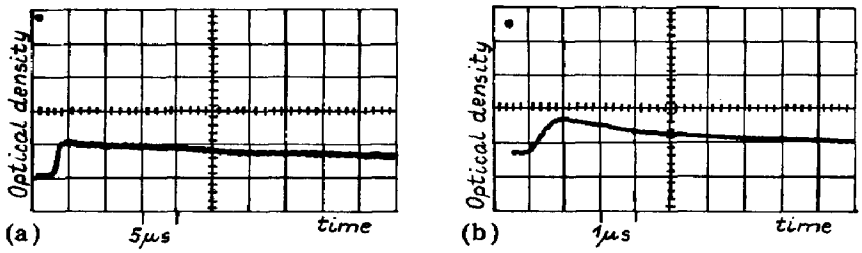


Fig. 4. Oscilloscope traces for the decay of the triplet intermediate in laser flash photolysis: transient absorption ($T_1 \rightarrow T_n$) signals of anthracene ($c = 3 \times 10^{-3}$ M) in (a) the absence and (b) the presence of the N-chelate (A) isomer of PH ($c = 6 \times 10^{-5}$ M) in deoxygenated 95% EtOH (T = 293 K; λ = 420 nm).

was $\tau_{T_1} = 0.6 \times 10^{-4}$ s (Fig. 4). For A in 95% EtOH $E_{S_1} = 65 \pm 2$ kcal mol^{-1} and $E_{T_1} = 40 \pm 2$ kcal mol^{-1} [19] so on energy grounds both singlet–singlet and triplet–triplet energy transfer to A are possible. For anthracene the ratio τ_{S_1}/τ_{T_1} is less than 10^{-4}, so if A were used in concentrations between 5×10^{-5} and 2.5×10^{-4} M only triplet–triplet energy transfer would occur. However, under these conditions the transfer of energy to A is not the only possible channel of deactivation of triplet anthracene. The rate constant k_q of energy transfer, the quenching constant K and the energy transfer efficiency for the A concentrations considered were obtained from the lifetimes $\tau_{T_1}{}^0$ and τ_{T_1} of anthracene in the triplet state measured in the absence and in the presence respectively of A (eqn. (5)) at the same concentrations as those used in the triplet–triplet-sensitized A → B photoisomerization (Fig. 4).

The calculated values are $K = 78\,000$ M^{-1} and $k_q = 1.7 \times 10^9$ M^{-1} s^{-1}, while the triplet–triplet energy transfer efficiency is between 40% and 90%. Under the conditions described, sensitized A → B isomerization is found to occur via energy transfer to A in the T_1 state. This is shown by the fact that the changes in the UV and CD spectra (Fig. 5), the positions of the isosbestic points and the linear ED diagrams are identical with those found in the direct isomerization experiments. In the sensitized isomerization, the incident radiation with λ = 254 mm is absorbed by anthracene only. At the anthracene concentrations used ($c = 3 \times 10^{-3}$ M) and the intensity of the radiation absorbed ($I_{abs} = 2 \times 10^{15}$ quanta s^{-1} cm^{-3}), the decay of triplet anthracene by either T_1–T_1 annihilation [43] or self-quenching [43] need not be taken into account. Also, energy transfer from anthracene in the T_2 state to A could be neglected because for anthracene $\tau_{T_2} \approx 10^{-11}$ s [44]. Since reabsorption of anthracene fluorescence by A was unavoidable, some direct A → B photoisomerization took place in the system. The contribution of the latter process to the experimentally measured A → B photoisomerization quantum yield was determined exactly [45] and was taken into account in the calculations of the limiting quantum yield $\phi_{A \rightarrow B}{}^{sens}$ for the triplet–triplet-sensitized isomerization. When the energy transfer yields obtained in the laser flash photolysis system were used, the calculated value was $\phi_{A \rightarrow B}{}^{sens} = 0.16 \pm 0.03$. In these calculations a value of $\phi_{S,T} = 0.71$ was employed for anthra-

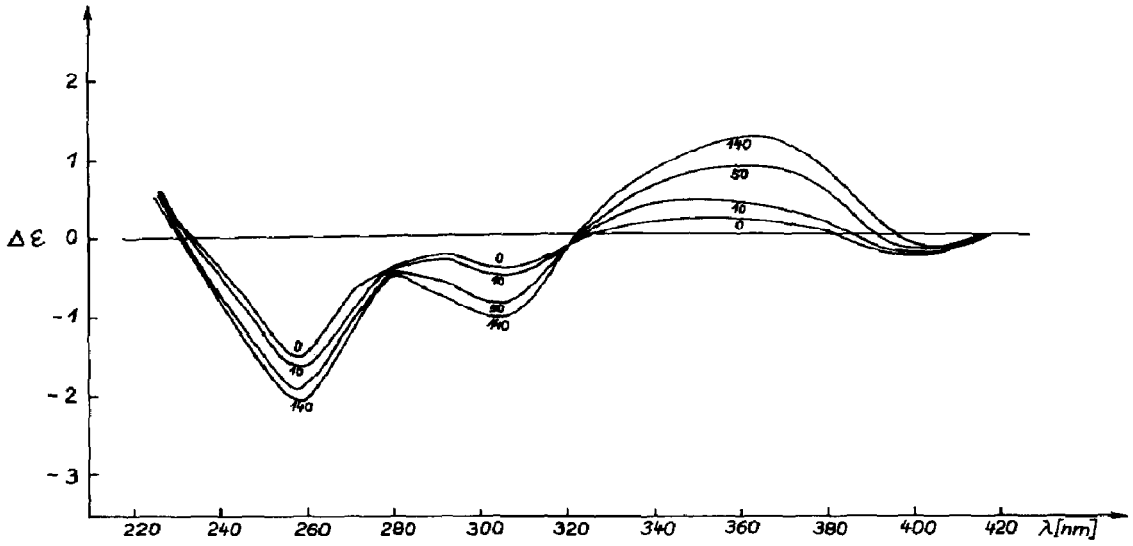


Fig. 5. Spectral changes in the CD spectra after the N-chelate → O-chelate (**A** → **B**) isomerization of PH ($c = 1 \times 10^{-4}$ M) photosensitized with anthracene ($c = 3 \times 10^{-3}$ M) in 95% EtOH by irradiation at $\lambda = 254$ nm and $T = 293$ K. The numbers on the curves give the irradiation time in seconds.

cene [24, 26, 29]. A similar value of $\phi_{A \to B}^{sens} = 0.15 \pm 0.03$ was obtained from the linear dependence of $1/\phi_{A \to B}^{app}$ on $1/[A]$ (Fig. 6) by extrapolation to $1/[A] \to 0$. The values of K and k_q calculated from steady state experiments, assuming $\tau_{T_1} = 0.6 \times 10^{-4}$ s for anthracene, were $K = 60\,000$ M^{-1} and $k_q = 1 \times 10^9$ M^{-1} s^{-1}. This confirms that **A** → **B** isomerization of PH sensitized by anthracene occurs by triplet–triplet energy transfer.

The photostationary state ratio $([A]/[B])_s^{sens}$ obtained is 0.85. Thus if we assume that E_{T_1}(anthracene) is about 3 kcal mol^{-1} higher than the E_{T_1} values of the **A** and **B** isomers (which has been experimentally proved for the **A** isomer), eqn. (6) is valid. The value of $\phi_{B \to A}^{sens}$ calculated from this equation is given in Table 3 which also includes the quantum yield of **A**

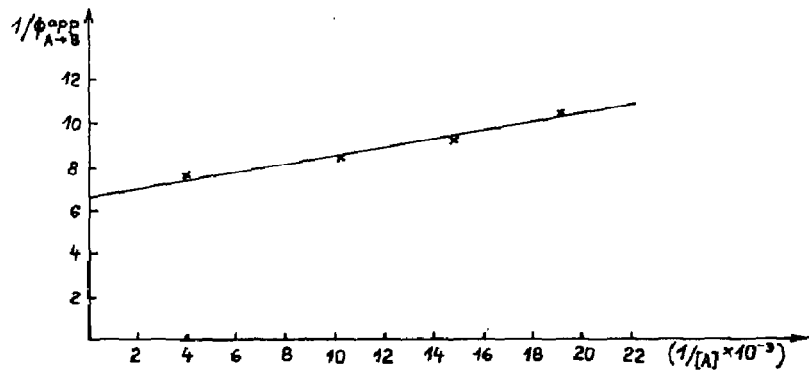


Fig. 6. The N-chelate → O-chelate (**A** → **B**) isomerization of PH photosensitized by anthracene.

TABLE 3

Quantum yields $\phi_{A\to B}$ and $\phi_{B\to A}$ of A → B photoisomerization of PH, quantum yield ϕ_A of A photolysis and the position of the photostationary state $([A]/[B])_s$ for direct and sensitized isomerization

Mechanism of isomerization	$\phi_{A\to B}$	$\phi_{B\to A}$	$([A]/[B])_s$	λ_{irr} (nm)	ϕ_A
Direct[a]	0.031 ± 0.004	—	0.053 ± 0.02	436	$(5 \pm 1)\times 10^{-4}$
Direct[a]	0.029 ± 0.005	0.025 ± 0.005	0.32 ± 0.03	418	—
Direct[a]	0.059 ± 0.004	0.18 ± 0.03	1.90 ± 0.2	254	—
Sensitized[b] $S_1 \to {}^1p^*$	0.48 ± 0.08	0.52[c]	1.1 ± 0.2	476.5	$<(1.7 \pm 0.4)\times 10^{-4}$
Sensitized[d] $T_1 \to T_1$	0.16 ± 0.03	0.14[c]	0.85 ± 0.16	254	$(2 \pm 0.5)\times 10^{-3}$

[a] Taken from ref. 15.
[b] Tetracene as sensitizer.
[c] Calculated from eqn. (6).
[d] Anthracene as sensitizer.

isomer photolysis sensitized by anthracene as determined from the UV and CD spectra.

In order to determine whether the triplet–triplet-sensitized A → B isomerization occurs via the twisted spectroscopically unobserved $^3p^*$ triplet state of PH we used perylene as a sensitizer (E_{T_1} = 35 kcal mol^{-1} [24]). Energy transfer between T_1(perylene) and T_1(A) was impossible in these experiments. This was supported by the observation of total quenching of the $T_1 \to T_n$ transient absorption signal of A by azulene ($c = 5 \times 10^{-3}$ M) for which $E_T = 39 \pm 2$ kcal mol^{-1} [46]. When deoxygenated solutions of perylene ($c = 1.5 \times 10^{-4}$ M) and of A ($c = (5 - 25) \times 10^{-5}$ M) in 95% EtOH were irradiated at $\lambda = 436$ nm, A → B isomerization was found to occur possibly as a result of T_1(perylene) → $^3p^*$(PH) energy transfer [47].

Owing to the limited solubility of perylene in 95% EtOH part of the incident radiation (about 10%) was absorbed by A. The contribution of A absorption was calculated from the expression [48]

$$I_{abs}{}^{A} = I_0 \frac{\epsilon_A c_A}{\epsilon_A c_A + \epsilon_p c_p} \{1 - 10^{-(\epsilon_A c_A + \epsilon_p c_p)l}\} \tag{7}$$

where ϵ_A and c_A, and ϵ_p and c_p are the molar absorption coefficients and concentrations for A and perylene respectively, l is the thickness of the cuvette and I_0 is the intensity of the incident radiation. However, direct isomerization contributed only part of the experimentally observed A → B reaction yield.

4. Discussion

4.1. Direct photoisomerization

For isomer A, $\phi_{A\to B} \gg \phi_A$ and the photoisomerization rate is considerably greater than the thermal isomerization rate [15]. Thus the photo-

isomerization process can be studied until the photostationary state is reached with no other chemical reactions interfering.

No influence of the concentration of A within the range 10^{-3} - 10^{-6} M or of the intensity of absorbed radiation between 1×10^{15} and 1×10^{17} quanta s^{-1} cm^{-3} on $\phi_{A \rightarrow B}$ and $([A]/[B])_s$ was observed, indicating that direct isomerization is an intramolecular process. This conclusion is also supported by the lack of effect of the free-radical scavenger on $\phi_{A \rightarrow B}$ and $([A]/[B])_s$. However, in contrast with the observations of the rate of thermal isomerization [21], the lack of influence of polarity and basicity of the solvent on $\phi_{A \rightarrow B}$ proves that photoisomerization does not occur through excited states with charge transfer or ionic structures. This is consistent with the observation of only slight effects of solvent properties on the UV, CD and fluorescence spectra of the A isomer [21, 49].

In a previous paper [15], the quantum yields of the A → B and particularly the B → A isomerization reactions were shown to depend on the wavelength of the radiation absorbed. The photostationary state position $([A]/[B])_s$ was found to depend on the molar absorption coefficients ϵ_A and ϵ_B at the wavelength of irradiation and on the quantum yield of direct photoisomerization. The experimental results obeyed the relation [15, 50]

$$\left(\frac{[A]}{[B]}\right)_s = \frac{\epsilon_B}{\epsilon_A} \frac{\phi_{B \rightarrow A}}{\phi_{A \rightarrow B}} \tag{8}$$

This proves that A → B photoisomerization occurs via a common excited state. The following is evidence that this is a singlet state.

(1) A very small quantum yield of intersystem crossing for A is obtained ($\phi_{S,T} = 6 \times 10^{-3}$) and the quantum yield of triplet–triplet-sensitized A → B isomerization is $\phi_{A \rightarrow B}^{sens} = 0.16$. Thus the contribution of the triplet state to the direct isomerization is less than 2%.

(2) The $T_1 \rightarrow T_n$ transient absorption of A disappears completely in the presence of azulene ($c = 5 \times 10^{-3}$ M) or oxygen, whereas the influence of azulene or oxygen on $\phi_{A \rightarrow B}$ is slight. However, the effect of azulene and oxygen on A → B photoisomerization is caused only by the quenching of the A isomer in the $^1A^*$ state, as shown by identical linear Stern–Volmer dependences for the quenching of both A → B isomerization and A isomer fluorescence.

(3) A solvent such as ethyl iodide which contains external heavy atoms has no effect on $\phi_{A \rightarrow B}$.

The results of the photoisomerization of PH sensitized by tetracene imply that this reaction occurs via a twisted singlet state $^1p^*$. The minimum energy in this state could correspond to the rotation of the H—N—C_6H_5 fragment about the C(2)=N bond to a position perpendicular to the remainder of the molecule. From the measurements of the A → B isomerization of PH sensitized with tetracene, $\phi_{A \rightarrow B}^{sens}$ is 0.48. This should be compared with the value of 0.52 for $\phi_{B \rightarrow A}^{sens}$ calculated from eqn. (6). Such results are evidence that, owing to energy transfer from tetracene to A and B isomers, the latter undergo deactivation solely through a common excited state (*i.e.*

$\phi_{A \to B}^{sens} + \phi_{B \to A}^{sens} = 1$) which has properties consistent with those of the twisted excited state $^1p^*$ [1 - 3, 5]. The suggestion that this may be a state of perpendicular configuration with its minimum energy at a twisting angle of 90° follows from the position of the photostationary state ($([A]/[B])_s^{sens} = 1.1 \pm 0.2$). However, A → B isomerization does not occur directly from the $^1A^*$ state for the following reasons.

(1) The difference in energy E_{S_1}(tetracene) $- E_{S_1}$(A) is -5 kcal mol^{-1} but the value of k_q for quenching of the tetracene fluorescence and sensitized A → B isomerization is 5×10^9 M^{-1} s^{-1} (see above).

(2) Fluorescence from $^1A^*$ cannot be sensitized by energy transfer from tetracene.

(3) The values of $\phi_{A \to B}$ found for direct isomerization ($\phi_{A \to B} = 0.03$) are very different from those for isomerization sensitized with tetracene ($\phi_{A \to B}^{sens} = 0.48$). If energy transfer occurred from tetracene to $^1A^*$ these quantum yields should be the same.

On the basis of the experimental results obtained, direct A → B photoisomerization of PH can be represented by a scheme analogous to that for the *cis–trans* isomerization of stilbene and its derivatives [1 - 3, 6]:

$$^1A \xrightarrow{h\nu} {}^1A^* \tag{9}$$

$$^1A^* \xrightarrow{k_d} {}^1A \tag{10}$$

$$^1A^* \xrightarrow{k_{^1A^*,\,^1p^*}} {}^1p^* \tag{11}$$

$$^1p^* \xrightarrow{k_{kW}} {}^1p \tag{12}$$

$$^1p \xrightarrow{k_{^1p,\,^1A}} \alpha\,{}^1A \tag{13}$$

$$^1p \xrightarrow{k_{^1p,\,^1B}} (1-\alpha)\,{}^1B \tag{14}$$

In this scheme ^1p denotes the ground state of PH in the twisted configuration, k_d is the sum of rate constants of deactivation of the excited singlet state $^1A^*$ with no changes in the geometry of A and $k_{^1A^*,\,^1p^*}$ is the rate constant of radiationless transition (rotation) [40] to the $^1p^*$ state. A twisted molecule undergoes internal conversion with no change in its geometry from the $^1p^*$ state to ^1p with a rate constant k_{kw} [1, 6] followed by a transition to A and B isomers with planar configuration with an efficiency $\alpha \approx (1 - \alpha) \approx 0.5$.

The singlet–singlet isomerization of A sensitized by tetracene (S) can be illustrated by the following scheme:

$$^1S \xrightarrow{h\nu} {}^1S^* \tag{15}$$

$$^1S^* + {}^1A \rightarrow {}^1S + {}^1p^* \tag{16}$$

followed by processes (12) - (14) as in direct isomerization. The endothermic energy transfer to the spectroscopically observed $^1A^*$ state of planar configuration is impossible for energetic reasons. However, a change in the geometry of A is possible in its ground electronic state. The change could occur by torsional and bending vibrations, which should serve as primary acceptors of electronic energy, and also as a result of interaction with the polar solvent (DMSO) [51, 52]. Such a change can decrease the value of the energy required for the excitation of A to $^1p^*$ which could make energy transfer (reaction (16)) possible. The configuration of $^1p^*$ could also be attained in an encounter complex formed by the interaction of tetracene with A followed by energy transfer according to the scheme [1, 2, 53]

$$^1S^* + {}^1A \xrightarrow{k_a} {}^1S^* \cdots {}^1A \tag{17}$$

$$^1S^* \cdots {}^1A \xrightarrow{k_b} {}^1S^* + {}^1A \tag{18}$$

$$^1S^* \cdots {}^1A \xrightarrow{k_c} {}^1S + {}^1p^* \tag{19}$$

Provided that the system is in equilibrium, the following relation is valid:

$$k = \frac{k_a k_c}{k_b + k_c} \tag{20}$$

For $k_c \gg k_b$, $k = k_a$ and the process of energy transfer should be diffusion controlled. Such a scheme (processes (17) - (20)) can explain the unexpectedly high value of the rate constant k_q for energy transfer from tetracene to A ($k_q = 5 \times 10^9$ M^{-1} s^{-1}). This value, however, was obtained by assuming that $\tau_{S_1} = 6 \times 10^{-9}$ s for tetracene in DMSO, *i.e.* the same value as for tetracene in C_6H_{12} and EtOH [24], which may not be valid.

The results obtained for A → B isomerization sensitized by tetracene under the assumption that eqn. (6) is valid imply that $\phi_{A \to B} + \phi_{B \to A} = 1$. Therefore it follows that a PH molecule in the twisted configuration decays from the excited $^1p^*$ state only by the process of rapid radiationless decay (A–B photoisomerization). Thus a small value of $\phi_{A \to B}$ in direct isomerization may be related to a small quantum yield of the process

$$^1A^* \xrightarrow{k_{^1A^*,\,^1p^*}} {}^1p^*$$

This, in turn, may result from the existence of an energy barrier to the radiationless transition $^1A^* \to {}^1p^*$ [40], the occurrence of which may be caused by the presence of a quasi-aromatic ring [54] and an intramolecular hydrogen bond [21, 55] which hinder the change in the geometry of an A molecule. This conclusion is supported by a significant temperature effect on the quantum yield of direct photoisomerization ($\phi_{A \to B}$ is 0.03 at room temperature while at 77 K it is 1×10^{-3} for λ_{irr} = 436 nm (Section 3.1)) and by the simultaneous significant increase in the intensity of fluorescence of the A isomer with decreasing temperature.

It follows from the preceding data that $\phi_{A \to B}$ for direct isomerization can be written

$$\phi_{A \to B} = \phi_{^1A^* \to {}^1p^*}(1 - \alpha) = k_{^1A^*, {}^1p^*}\tau_{^1A^*}(1 - \alpha) = A_{AP} \exp\left(-\frac{E_{AP}}{RT}\right) \tau_{^1A^*}(1 - \alpha) \tag{21}$$

while the lifetime τ of the A isomer in the excited singlet state $^1A^*$ is given by

$$\tau_{^1A^*} = \frac{1}{k_d + k_{^1A^*, {}^1p^*}} \tag{22}$$

where A_{AP} is the pre-exponential factor, E_{AP} is the activation energy for the twisting step $^1A^* \to {}^1p^*$ and R is the gas constant. Since $\phi_{A \to B}{}^{sens} = 0.48$ and $\phi_{A \to B} = 0.031$ for $\lambda_{irr} = 436$ nm [15], according to the scheme (processes (9) - (16)) the quantum yield of the transition $^1A^* \to {}^1p^*$ calculated from

$$\phi_{^1A^* \to {}^1p^*} = \frac{\phi_{A \to B}}{\phi_{A \to B}{}^{sens}} \tag{23}$$

is $\phi_{^1A^*, {}^1p^*} = 0.064$. Since we know the value of $\phi_{^1A^* \to {}^1p^*}$ and $\tau_{^1A^*}$ is taken as 4.5×10^{-9} s [19], the rate constant of twisting in the excited singlet state from the $^1A^*$ configuration to the perpendicular $^1p^*$ configuration can be obtained from eqn. (21).

The value of 1.4×10^7 s^{-1} obtained for $k_{^1A^*, {}^1p^*}$ is relatively small [1 - 3, 56] which may indicate that the quasi-aromatic ring and the intramolecular hydrogen bond N—H···N play an important role in the conservation of the planar configuration of A and hinder the NHC_6H_5 group rotation about the C(2)=N bond. The measured value of $\phi_{A \to B}$ was independent of viscosity considering the low value of $k_{^1A^*, {}^1p^*}$. However, the viscosity does have a significant effect on the rate of the fast rotation of molecular fragments in radiationless transitions ($k \approx 10^{-10}$ s^{-1}). In such cases the viscosity apparently influences the height of the energy barrier to rotation [1, 57]. This suggestion has been confirmed for the *cis–trans* isomerization of stilbene by picosecond laser spectroscopy [4, 56].

The $^1p^*$ state, which has a perpendicular configuration analogous to that of PH, has been suggested to contribute to the *cis–trans* isomerization reactions of stilbene [1, 2, 4, 5, 40, 58] and its derivatives [3, 6], azobenzene [59] and the phenylhydrazones [9, 11, 12].

An upper limit to the lifetime of the $^1p^*$ state of PH was calculated using the observation that even for the largest oxygen concentration used only the $^1A^*$ state is quenched (Section 3.2). If it is assumed that the measurement error is ±15% (eqn. (1)) and that the rate of quenching of the $^1p^*$ state is diffusion controlled [1, 2, 60], the estimated lifetime $\tau_{^1p^*}$ is less than 1×10^{-9} s.

4.2. Triplet–triplet-sensitized isomerization

Since the quantum yield of intersystem crossing $S_1 \to T_1$ is very small ($\phi_{S,T} = 6 \times 10^{-3}$ for A), the direct isomerization reaction rarely occurs

through the excited triplet states. However, it could occur following triplet–triplet energy transfer. In the case of A → B isomerization sensitized by anthracene the measured value of the limiting quantum yield $\phi_{A \to B}^{sens}$ is 0.16 and the value of $\phi_{B \to A}^{sens}$ calculated from eqn. (6) is 0.14. The relatively small total value $\phi_{A \to B}^{sens} + \phi_{B \to A}^{sens} = 0.30$ may result from the quantum yield of the radiationless transition $^3A^* \to {}^3p^*$ being less than unity and possibly from energy wastage processes between the sensitizer and A [53, 61]. A possible scheme describing triplet–triplet-sensitized A → B isomerization is given below [1, 6]:

$$^1S \xrightarrow{h\nu} {}^1S^* \xrightarrow{k_{S,T}} {}^3S^* \tag{24}$$

$$^3S^* \xrightarrow{k_1} {}^1S \tag{25}$$

$$^3S^* + {}^1A \xrightarrow{k_2} {}^1S + {}^3A^* \tag{26}$$

$$^3A^* \xrightarrow{k_{^3A^*,{}^3p^*}} {}^3p^* \tag{27}$$

$$^3A^* \xrightarrow{k_4} {}^1A \tag{28}$$

$$^3p^* \xrightarrow{k_5} {}^1p \tag{29}$$

$$^1p \xrightarrow{k_6} \alpha\,{}^1A \tag{30}$$

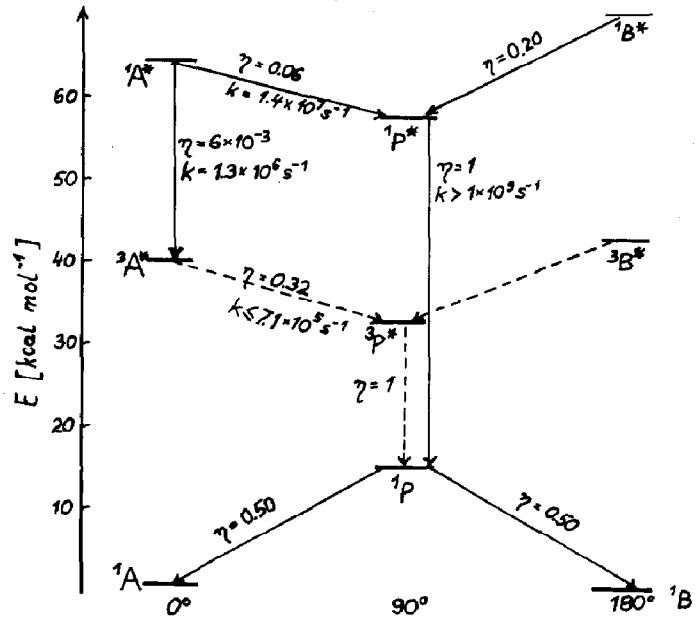
$$^1p \xrightarrow{k_7} (1-\alpha)\,{}^1B \tag{31}$$

where S denotes the sensitizer, $^3A^*$ denotes the A isomer in the planar configuration of the triplet state, ^1p is the ground electronic state of PH in the perpendicular configuration and asterisks indicate excited states. The scheme is consistent with the results of A → B isomerization sensitized by perylene and methylene blue [62] which occurs via a spectroscopically unobserved twisted $^3p^*$ state.

Under the conditions of total energy transfer from high energy sensitizers to A (process (26)), taking into account the $\phi_{S,T}$ value of the sensitizer, the limiting quantum yield $\phi_{A \to B}^{sens}$ of the sensitized A → B isomerization can be expressed as

$$\phi_{A \to B}^{sens} = \phi_{^3A^* \to {}^3p^*}(1-\alpha) = k_{^3A^*,{}^3p^*}\tau_{^3A^*}(1-\alpha) \tag{32}$$

If it is assumed that the above scheme (processes (24) - (31)) adequately describes the experimental results obtained and the values $\phi_{A \to B}^{sens} = 0.16$, $\tau_{^3A^*} = 4.5 \times 10^{-7}$ s [19] and $1-\alpha = \alpha = 0.5$ are used, the following values can be calculated: $\phi_{^3A^* \to {}^3p^*} = 0.32$ and $k_{^3A^*,{}^3p^*} = 7.1 \times 10^5\ s^{-1}$. The $^3p^*$ state has also been found to contribute to the photoisomerization of styrene and the azomethine dyes [46].



Angle of twist of NHC_6H_5-fragment about C_2=N bond in PH osazone.

Fig. 7. Schematic representation of the electronic states, the efficiencies η and the rate constants k of the transitions involved in the direct (———) and triplet–triplet-sensitized (— — —) N-chelate → O-chelate (**A** → **B**) photoisomerization of PH at λ = 405 nm. The energies of the electronic states are determined with an accuracy to better than ±3 kcal mol^{-1} [15, 19, 49]. The energies of the ^{1}**B*** and ^{3}**B*** states are tentatively assigned.

On the grounds of the results obtained, the electronic energy levels involved, their contributions to the **A** → **B** photoisomerization of PH [19] and the transitions between them can be represented by the scheme shown in Fig. 7. The efficiency η of a step is defined as the ratio of the rate constant k of that step to the sum of the rate constants of depopulation of that excited state [41, 63]. The values of η and k for **A** → **B** isomerization in the triplet state were calculated by assuming that the process occurs only via the ^{3}p* state (Fig. 7). The efficiency η was used instead of the quantum yield to stress the relative importance of each deactivation process in the isomerization reaction.

It follows from the results obtained that reversible **A** → **B** isomerization may be an important pathway for the radiationless deactivation of excited PH. However, the presence of the intramolecular hydrogen bonds N···H—N and O···H—N in the **A** and **B** isomers respectively causes a decrease in $\phi_{A \to B}$ similar to that observed for phenylhydrazones [9, 12] and simultaneously enhances the quantum yield of internal conversion for the planar configuration [1, 2, 46, 64].

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