

PHOTOCHEMISTRY AND PHOTOPHYSICS OF OSAZONES I: PHOTOCHEMICAL AND THERMAL ISOMERIZATION OF D-"ARABINO"-HEXULOSE PHENYLOSAZONE

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Summary

The photochemical and thermal N-chelate-O-chelate isomerization of D-"arabino"-hexulose phenylosazone (PH) in solution was studied. The rate constants and activation parameters for thermal isomerization were calculated. An obvious wavelength effect on the photoisomerization quantum yield and on the position of the photostationary state was observed. Direct photoisomerization is believed to occur via a common excited singlet state. PH was found to have photochromic properties. The photoisomerization reaction was proved to be a fast efficient method of synthesizing the O-chelate isomer of osazone.

1. Introduction

It has been known for several decades that osazones change their colour [1] on exposure to solar radiation as has been shown by corresponding changes in the UV absorption spectra [2]. However, no data concerning the photophysics and photochemistry of osazones are available in the literature. A number of workers [3 - 7] have reported that these compounds, which are mainly sugar derivatives, undergo a thermal isomerization reaction about one of the two C=N double bonds which is due to the temperature and basic solvent effects.

Photoisomerization about the C=N bond has been studied for some other classes of organic compounds [8]. The reaction is relatively well understood for phenylhydrazones and their derivatives which frequently exhibit photochromic properties [9 - 15]. However, much more attention has been focused on the isomerization about a C=C double bond in stilbenes and other aromatic hydrocarbons [16].

The interesting structural properties of osazones and their applicability as chemical stabilizers in analytical chemistry, colour photography and holography [17, 18] indicate that a detailed investigation of their photo-

chemical and photophysical properties in the excited states would be of importance.

A relatively simple compound representing osazones derived from sugars is D-“arabino”-hexulose phenylosazone (D-glucose phenylosazone) (PH). The structure and the mechanism of thermal isomerization (mutarotation) of this compound have been studied [3, 4, 6]. As PH exhibits optical activity, circular dichroism (CD) and polarimetric measurements can be performed in addition to UV spectrometry which enables its thermal and photochemical N-chelate–O-chelate isomerization and photolysis to be analysed accurately.

2. Experimental details

2.1. Materials

The N-chelate isomer of PH (A) was obtained using the method reported by Neuberger and Strauss [19] and Noyons [20]. Crystallized D-glucose (puriss, POCh) and phenylhydrazine or its hydrochloride (puriss, Fluka) were used as starting materials. The osazone obtained was repeatedly crystallized from 95% ethanol (EtOH) (fluorometric grade, Merck) and from doubly distilled water. Its melting point was $T = 485 - 486$ K. The results of elementary analysis were as follows: nitrogen, 15.66%; carbon, 59.80%; hydrogen, 6.05%. The UV, nuclear magnetic resonance (NMR), IR and mass spectra were consistent with the literature data [4, 21 - 27].

The O-chelate isomer B (Section 4) of PH was prepared photochemically with a yield of about 90% by irradiation of the N-chelate isomer A ($\lambda = 436$ nm). Thermal isomerization yielded approximately 10% of isomer B at equilibrium at room temperature. Owing to the thermal instability of B, its isolation from solution was impossible.

95% EtOH (fluorometric grade) was used as a solvent in the isomerization process with no further purification. The solvents used for the measurements of the optical rotation and of the UV and CD spectra were purified by distillation.

Actinometric determinations were performed using uranyl oxalate [28] and Reinecke's salt [29].

The UV and CD absorption spectra were calibrated using potassium dichromate (Hopkins and Williams), holmium perchlorate (BDH) and *epi*-androsterone (Roussel–Jouan) as standards.

2.2. Apparatus

The irradiation system used consisted of a light source, a lens system, a thermal filter, diaphragms, interference and absorption filters or a double-prism M-3 monochromator (Cobrabid) and cells aligned along an optical bench. A carousel system was also used. The quartz cuvettes were rectangular or cylindrical with a thickness of 0.1 - 5 cm and a diameter of 0.5 - 2.2 cm.

The radiation of wavelength 254 nm was obtained from a low pressure mercury lamp (TNN 15/32, Original Hanau). The radiation of wavelengths 313, 366, 377, 405, 418 and 436 nm was obtained from a high pressure mercury lamp (HBO-200, Narva) and from a xenon lamp (XBO-150, Osram) using interference filters (Carl Zeiss) and glass absorption filters (Schott). The intensity of the incident light at all wavelengths used was of the order of 10^{-6} - 10^{-7} einsteins min^{-1} .

The UV spectra were recorded using Specord UV-VIS (Carl Zeiss) and Cary 118 C (Varian) spectrometers. The CD spectra were obtained using a dichrograph mark III spectropolarimeter (Jobin-Yvon). The rotation of the optically active compounds was measured using a Polamat A polarimeter (Carl Zeiss). IR spectra were recorded using an SP-200 G spectrometer (Pye-Unicam) with KBr pellets or cuvettes containing EtOH. The NMR spectra were measured in deuterated dimethylsulphoxide (DMSO- d_6) using an EM-360 spectrometer (Varian) and the mass spectra were obtained using a JMS-D-100 spectrometer (Jeol). The elementary analysis was performed using a Perkin-Elmer model 240 analyser.

2.3. Procedure

In the studies of thermal and photochemical isomerization aerated or deoxygenated solutions containing 10^{-4} - 10^{-5} M of pure A or a mixture of the isomers containing about 90% B were investigated. The photoisomerization reaction was controlled by measuring the spectral changes in the UV and CD spectra in the range 220 - 500 nm.

The UV and CD spectra of B were calculated using the method proposed by Fischer [30] as the isomer could not be obtained with an efficiency of 100%. In order to calculate the yield $[B]_s$ of this isomer in a photostationary state produced by irradiation at $\lambda = 405$ nm, the following were used as the second wavelength: 254, 313, 366 and 377 nm. Consistent results were obtained at all these wavelengths which were chosen because, as required by the assumptions of Fischer's method [30, 31], the same value of $\phi_{A \rightarrow B} / \phi_{B \rightarrow A}$ was obtained for all of them (see Table 3 in Section 3.2).

The quantum yield of A-B isomerization and the composition of the photostationary state were calculated from the changes in the UV and CD spectra. In order to do this the spectra were recorded for irradiation times corresponding to a small percentage conversion (less than 15%) at and near the stationary state. The differential spectra were recorded in order to eliminate the changes due to thermal isomerization from the UV spectra when studying B \rightarrow A photoisomerization. Corrections for the back reaction [32], the thermal isomerization and the internal filter effect [33] were taken into account in the calculation of the quantum yield of B \rightarrow A photoisomerization. All the quantum yield values of A \rightarrow B photoisomerization were obtained by extrapolation to zero percentage conversion. The methods of Zimmerman *et al.* [34] and Blanc [35] were used to calculate the quantum yield of A \rightarrow B isomerization and the results obtained were similar.

The presence of five isobestic points in the UV spectrum and two isobestic points in the CD spectrum and the existence of a distinct photostationary state in the system indicated that only the photoisomerization reaction took place. This conclusion was confirmed by an experiment in which the solvent was evaporated after the photostationary state had been reached. During this process B was transformed into A so that only the latter existed in the solid state. The quantitative UV and CD spectra of the dissolved precipitate were identical with the spectra of freshly dissolved A. Also, the optical rotation conserved its initial value, *e.g.* $[\alpha]_D^{20} = -58^\circ$ in dimethylformamide.

The photolysis of both isomers occurred when the solutions were irradiated for longer times than required to reach the photostationary state. The quantum yields ϕ_A and ϕ_B of the photolysis of both isomers were obtained from the UV and CD spectra.

All the photochemical investigations were carried out at room temperature (293 ± 1 K). The solutions studied were deoxygenated by purging for 10 - 15 min with helium which had been passed through a column containing copper ($T = 463$ K) and type 4A molecular sieve. The concentration of oxygen under these conditions was determined by measuring the lifetime of triplet anthracene [36, 37] in a laser flash photolysis apparatus [38, 39] and was found to be less than 10^{-6} M.

The kinetics of thermal isomerization was determined from changes in the UV and CD absorption spectra with time at various wavelengths. In order to calculate the activation energy, the entropy and other activation parameters the changes in absorption were measured at different temperatures.

The results reported here are arithmetic means of at least three, and generally five, measurements. In most cases the error quoted is the r.m.s. of the average, but the systematic error is also included where necessary.

3. Results

3.1. Thermal isomerization

Measurements of the A-B thermal isomerization were carried out in the temperature range 293 - 323 K. The temperature dependences of the rate constants k_A and k_B of $A \rightarrow B$ and $B \rightarrow A$ thermal isomerization are presented in Tables 1 and 2 respectively. The linear dependence of $\ln\{E_0/(E_0 - E)\}$ on the time t was determined at each temperature considered. In this expression E_0 is the initial absorption at a given wavelength λ , E is the absorption at time t at the same wavelength and t is the time of reaction. These results show that the reaction is a first-order process.

Tables 1 and 2 also include the activation energy E_a , the entropy ΔS , the activation parameter A calculated from the dependence $\ln k = \ln A - E_a/RT$ where R is the gas constant, the ratio $([A]/[B])_s$ of the isomer concentrations in the stationary state and the half-life $\tau_{1/2}$ for the reactions $A \rightarrow B$ and $B \rightarrow A$.

TABLE 1

Rate constants and activation parameters for the thermal A → B isomerization of PH ($c = 5 \times 10^{-5}$ M) in 95% EtOH

Temperature (K)	$k_A \times 10^6$ (s ⁻¹)	E_a (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	$A \times 10^{-5}$ (s ⁻¹)	$([A]/[B])_s$	$\tau_{1/2} \times 10^{-3}$ (s)
293	4.9				7.3	4.6
298	10.1				8.3	
313	24.3	55.3	-163	4.1	12.0	
323	38.9				13.5	

TABLE 2

Rate constants and activation parameters for the thermal B → A isomerization of PH ($c = 5 \times 10^{-5}$ M) in 95% EtOH

Temperature (K)	$k_B \times 10^4$ (s ⁻¹)	E_a (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	$A \times 10^{-7}$ (s ⁻¹)	$\tau_{1/2} \times 10^{-3}$ (s)
298	1.3				7.8
313	4.25				
323	8.85	62.4	-108	1.1	

3.2. Photochemical isomerization

The measured UV spectrum of isomer A in 95% EtOH and the calculated spectrum of isomer B are shown in Fig. 1. The spectrum of isomer A does not show any deviation from the Lambert-Beer law at any concentration in the range 5×10^{-3} - 5×10^{-6} M. This confirms the presence in the solution of individual PH molecules which interact only slightly. The absorption spectra of this isomer are similar regardless of the solvent used (dioxan, EtOH, acetonitrile, dimethylformamide, glycerine or DMSO) and the maximum shift in the absorption maxima does not exceed 300 cm^{-1} [40, 41]. Because of this and the high intensities of the absorption bands (the molar absorption coefficient ϵ is greater than $5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) only π - π^* bands could be observed in the UV spectrum.

The CD spectra of both isomers are presented in Fig. 2. They provide valuable information for photochemical studies concerning the position of the lowest excited singlet state $^1A^*$ of isomer A. The absorption band corresponding to this state is masked in the UV spectrum (Fig. 1). The absorption maxima in the UV and CD spectra of A determined by resolving the spectra into single bands are satisfactorily consistent [41]. A and a mixture of A (10%) and B (90%) at concentrations between 3×10^{-5} and 5×10^{-5} M in 95% EtOH were irradiated at wavelengths of 436, 418, 405, 366, 313 and

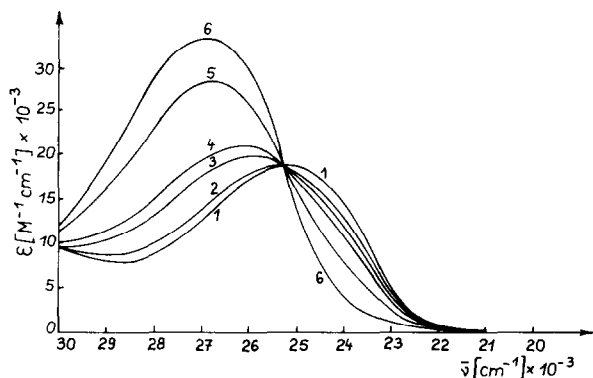


Fig. 1. UV spectra of PH in the photostationary state ($c = 5 \times 10^{-5}$ M) in 95% EtOH: curve 1, N-chelate isomer; curve 2, irradiated at $\lambda = 366$ nm; curve 3, irradiated at $\lambda = 313$ nm; curve 4, irradiated at $\lambda = 254$ nm; curve 5, irradiated at $\lambda = 418$ nm; curve 6, O-chelate isomer.

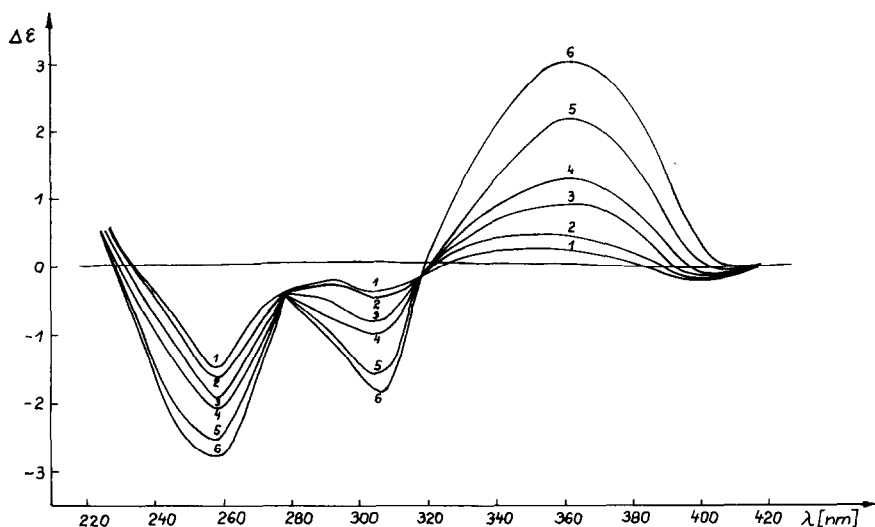


Fig. 2. CD spectra of PH in the photostationary state ($c = 5 \times 10^{-5}$ M) in 95% EtOH: curve 1, N-chelate isomer; curve 2, irradiated at $\lambda = 366$ nm; curve 3, irradiated at $\lambda = 313$ nm; curve 4, irradiated at $\lambda = 254$ nm; curve 5, irradiated at $\lambda = 418$ nm; curve 6, O-chelate isomer.

254 nm which correspond to excitation into the electronic states $S_1 - S_5$. The excitation caused A-B photoisomerization. The changes produced in the UV absorption spectrum as a result of this process under irradiation at $\lambda = 436$ nm are shown in Fig. 3. Figures 1 and 2 show the UV and CD absorption spectra corresponding to the photostationary state attained in the system after irradiation at the other wavelength mentioned.

Table 3 presents the values of the photoisomerization quantum yields $\phi_{A \rightarrow B}$ and $\phi_{B \rightarrow A}$ and the ratio $([A]/[B])_s$ of the concentrations of isomers A

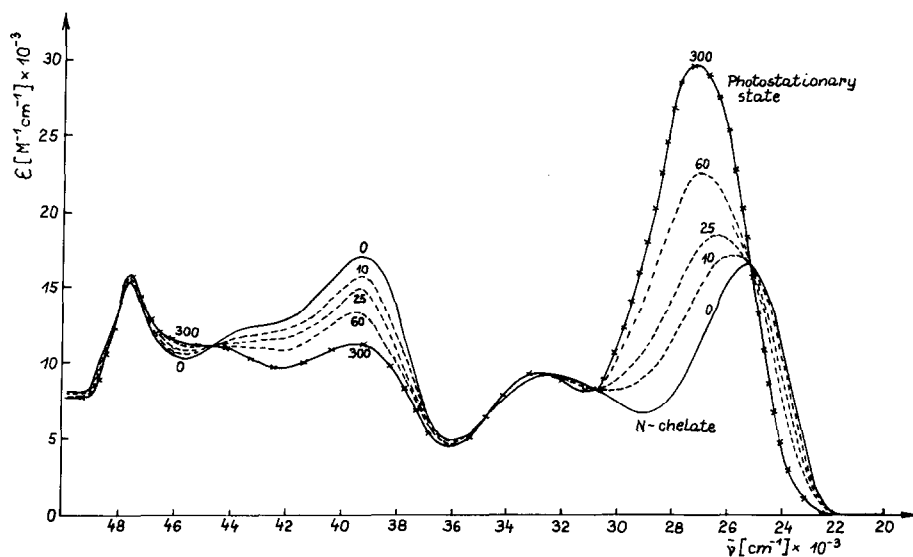


Fig. 3. Spectral changes in the UV spectra of the N-chelate isomer ($c = 5.6 \times 10^{-5}$ M) in 95% EtOH after photoisomerization under irradiation at $\lambda = 436$ nm ($T = 293$ K). The numbers on the curves give the irradiation time in seconds.

and B in the photostationary state calculated independently from the UV and CD spectra. The molar absorption coefficients ϵ_A and ϵ_B for both isomers at all the irradiation wavelengths and the quantum yields $\phi_{B \rightarrow A}^t$ of $B \rightarrow A$ photoisomerization calculated from the relation [30]

$$\phi_{B \rightarrow A}^t = \phi_{A \rightarrow B} \frac{\epsilon_A}{\epsilon_B} \left(\frac{[A]}{[B]} \right)_s \quad (1)$$

are also included in Table 3.

In the measurements of absorption in order to calculate ϵ_A and ϵ_B and in the photoisomerization reaction in order to obtain $([A]/[B])_s$ at a given wavelength, the same radiation sources and the same filters were used as were required to employ eqn. (1) in calculations of $\phi_{B \rightarrow A}^t$. In addition, to ensure that $\phi_{A \rightarrow B}$, $\phi_{B \rightarrow A}$ and $([A]/[B])_s$ depend only on the wavelength and not on the intensity of the absorbed light, the intensity in the range $0.5 \times 10^{16} - 1 \times 10^{17}$ photons $\text{cm}^{-3} \text{s}^{-1}$ for $\lambda = 366$ nm was shown not to affect the quantum yields of isomerization and the position of the photostationary state.

The position of the photostationary state under irradiation at a given wavelength was found to be independent of the initial concentration of both isomers. It was the same both in the case of irradiation at $\lambda = 366$ nm and when thermal isomerization occurred at 310 K. In contrast, irradiation at other wavelengths leads to a considerable increase in the content of B in the photostationary state (Table 3). However, in such cases after the photostationary state is attained and the irradiation stopped the system returns to the

TABLE 3

Effect of the wavelength λ on the quantum yields of photoisomerization $\phi_{A \rightarrow B}$ and $\phi_{B \rightarrow A}$ and on the photostationary ratio ($[A]/[B]$)_s^a

λ (nm)	$\phi_{A \rightarrow B}$	$\phi_{B \rightarrow A}$	$([A]/[B])_s$	$\Sigma\phi_{A \rightarrow B}$	$\phi_{B \rightarrow A}^f$	ϵ_A (M ⁻¹ cm ⁻¹)	ϵ_B (M ⁻¹ cm ⁻¹)	J_{abs}^b (quanta cm ⁻³ s ⁻¹)	$\Delta\lambda_{1/2}^c$ (nm)	$\frac{\phi_{A \rightarrow B}}{\phi_{B \rightarrow A}}$
254	0.059 ± 0.004	0.18 ± 0.03	1.90 ± 0.2	0.24	0.17	18800	12450	0.8 × 10 ¹⁶	1	0.31
313	0.046 ± 0.007	—	2.85 ± 0.3	0.19 ^d	0.14	10200	9800	0.5 × 10 ¹⁶	12	0.33
366	0.038 ± 0.004	0.14 ± 0.02	11.0 ± 1.0	0.17	0.13	11180	32750	0.8 × 10 ¹⁶	5.0	0.27
405	0.031 ± 0.004	0.10 ± 0.02	1.38 ± 0.1	0.13	0.085	15600	7850	1.5 × 10 ¹⁶	1.7	0.31
418	0.029 ± 0.005	0.025 ± 0.005	0.32 ± 0.03	0.054	0.025	12420	4610	5 × 10 ¹⁶	10	1.16
436	0.031 ± 0.004	—	0.053 ± 0.02	0.04 ^d	0.008	2450	480	5 × 10 ¹⁶	2.5	—

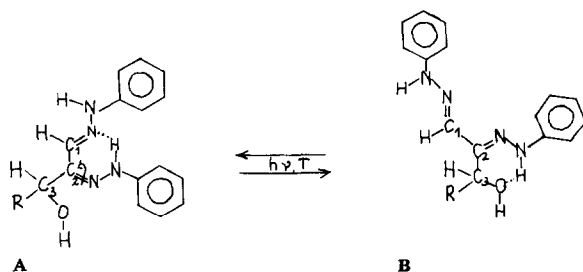
^a In deoxygenated 95% EtOH ($c = 5 \times 10^{-5}$ M).^b J_{abs} is the absorbed light intensity.^c $\Delta\lambda_{1/2}$ is the spectral width of the light.^d The value $\phi_{B \rightarrow A}^f$ was employed in the calculations.

stationary state characteristic of thermal isomerization with a rate constant $k_B = 1.3 \times 10^{-4} \text{ s}^{-1}$ ($T = 298 \text{ K}$).

The quantum yields ϕ of photolysis obtained from the changes in the CD and UV spectra on irradiation at $\lambda = 436 \text{ nm}$ are $\phi_A = 1 \times 10^{-4}$ and $\phi_B = 3 \times 10^{-4}$. The quantum yields of photolysis evidently depend on the wavelength of the radiation absorbed, *e.g.* for $\lambda = 254 \text{ nm}$ ϕ_A is 2×10^{-3} . However, since ϕ_A is much less than $\phi_{A \rightarrow B}$ for the irradiation times required to reach a photostationary state, almost no photolysis occurs. This is confirmed by the observation of a constant absorption value at the isosbestic points for both isomers at the following wavelengths: 223, 283, 308, 325, 396 nm in the UV spectrum and 278 and 323 nm in the CD spectrum. The positions of the isosbestic points in the UV and CD spectra are found to be the same for both thermal isomerization and photoisomerization. Also, the changes in the absorption in the UV and CD spectra at several of the wavelengths chosen show linear extinction difference (ED) diagrams of identical character [42] for both thermal and photochemical isomerization. However, the thermal isomerization rate is considerably lower than that of photochemical isomerization. For example, when PH was irradiated at $\lambda = 254 \text{ nm}$, the photostationary state (66% A and 34% B) was attained after 180 s and 40 s for $A \rightarrow B$ and $B \rightarrow A$ photoisomerization respectively, while the thermal isomerization efficiencies achieved within the same time were 0.1% and 0.4% respectively at a temperature of 293 K.

4. Discussion

The thermal and photochemical N-chelate-O-chelate (A-B) isomerization of PH is a consequence of a reversible change in the structure according to the following reaction [3, 4, 6, 43]:



where $R \equiv (\text{HCOH})_2\text{CH}_2\text{OH}$.

The reaction can be described as the rupture of the chelate structure $\text{N}-\text{H} \dots \text{N}$ and the formation of the $\text{N}-\text{H} \dots \text{O}$ structure. This is a result of the rotation of the $\text{HN}-\text{C}_6\text{H}_5$ group about the $\text{C}(2)=\text{N}$ bond after the intramolecular hydrogen bond $\text{NH} \dots \text{N}$ (or $\text{NH} \dots \text{O}$) has been broken. The same mechanism for both isomerization processes is confirmed by the observation of identical UV and CD spectra for the same percentage conversion, *i.e.* the

position of the isobestic points and the shapes of the linear ED diagrams are identical [42].

It follows from the results obtained (Tables 1 and 2) that thermal A \rightarrow B isomerization is an exothermic process. The increase in temperature shifts the stationary state towards the A isomer. The higher value of the rate constant $k_{B \rightarrow A}$ compared with $k_{A \rightarrow B}$ in thermal isomerization results mainly from the change in entropy during this process. The values of the activation energy calculated for PH ($E_a = 55.3 - 62.4 \text{ kJ mol}^{-1}$ for A-B thermal isomerization) are very similar to the values obtained for the phenylhydrazones [9, 44]. The latter compounds have also been found to show photochromic properties.

Since the rate of A-B photoisomerization is considerably greater than that of thermal isomerization and the quantum yields of the former are considerably higher than those of photolysis [38, 43], the photoisomerization process could be studied until the photostationary state was reached with no competitive reactions.

The quantum yield ϕ_{ISC} of the intersystem crossing for isomer A measured using the method of Bensasson *et al.* [45] and Porter and Topp [46] in the laser flash photolysis system is 6×10^{-3} [38, 40]. If a similar value is determined for isomer B the A-B photoisomerization is seen to occur only via the excited singlet states. Good agreement between the theoretical (eqn. (1)) and experimental values of $\phi_{B \rightarrow A}$, an almost constant value of $\phi_{A \rightarrow B}/\phi_{B \rightarrow A} = 0.30$ over a wide range of wavelengths [30] and the ϕ_{ISC} value of 6×10^{-3} for the A isomer indicate that A-B photoisomerization occurs through a common excited singlet state. This state may be the twisted state 1p which was in some cases proved to be involved in photoisomerization reactions [16, 47].

The results obtained together with the assumptions made provide the basis for proposing a mechanism of A-B photoisomerization analogous to that reported by Condorelli and coworkers [13 - 15] for phenylhydrazones and their derivatives:



The twisted configuration represents the minimum in the potential energy surface of the excited singlet states from which the molecules decay to the A and B forms in the ratio $\alpha/(1 - \alpha)$.

The results given in Table 3 illustrate the influence of wavelength on the quantum yields of photoisomerization, particularly for the B \rightarrow A reaction. The quantum yields are the greatest for the absorption at $\lambda = 254$ nm which corresponds to the excitation of the S₄ or S₅ state [41]. This is consistent with the proposition that the absorption of higher energy quanta results in a higher vibrational energy being deposited in torsional vibrations of the C=N bond which should serve as the primary acceptor of electronic energy [48 - 50]. This different value of the excitation can cause a different efficiency of the rotation of the NHC₆H₅ group about the double bond C(2)=N which would correspond to the transition through the energetic barrier in horizontal radiationless transitions (processes (3) and (6)) [16, 47, 49 - 51].

The intramolecular hydrogen bonds N \cdots HN (isomer A) and O \cdots HN (isomer B) hinder the rotation of the NHC₆H₅ group about the C(2)=N bond and simultaneously can increase the rate of internal conversion (processes (4) and (7)) [52]. This can essentially influence the relatively small values of $\phi_{A \rightarrow B}$ and $\phi_{B \rightarrow A}$, in particular at the excitation to the S₁ state: $\phi_{A \rightarrow B} = 0.031$ and $\phi_{B \rightarrow A} = 0.025$. Let us mention for comparison that the quantum yields of *syn-anti* isomerization for the compounds where the rotation of the NHC₆H₅ group also occurs about a C=N bond but which have no intramolecular hydrogen bonds are significantly greater, e.g. $\phi_{syn-anti} = 0.2 - 0.5$ [12, 14]. The values of $\phi_{A \rightarrow B}$ and $\phi_{B \rightarrow A}$ obtained for PH isomerization are similar to those reported for phenylhydrazones with an intramolecular or intermolecular hydrogen bond [10, 53]. A significantly greater value of $\phi_{B \rightarrow A}$ than $\phi_{A \rightarrow B}$ for PH at most of the wavelengths can result from the presence of a quasi-aromatic ring (resonance energy, about 40 kJ mol⁻¹ in the ground state) [3, 54], i.e. from the greater energetic barrier to rotation as far as isomer A is concerned. A similar dependence has been obtained for phenylhydrazone derivatives [10, 53]. Since $\phi_{A \rightarrow B} + \phi_{B \rightarrow A}$ is less than unity (Table 3), other processes in addition to isomerization are also found to take place in the deactivation of the excited A and B isomers and their contribution increases with a decrease in the energy of the quanta absorbed.

The results concerning the effect of temperature and wavelength on the isomerization reaction A-B (Tables 1 - 3) enable the photochromic properties of PH to be proved. According to these results photoisomerization can be a fast and efficient method of synthesizing the B isomer of PH which otherwise can be formed only slowly and with a very small yield in the thermal reaction.

The significant increase in the quantum yield of photolysis of A on excitation to higher electronic levels is analogous to that obtained by Binkley [55] for phenylhydrazones.

Studies of the effects of solvent, temperature, concentration and the presence of sensitizers and quenchers as well as measurements of the lifetimes of the S₁ and T₁ excited states have been performed to gain better insight into the mechanism of the A-B isomerization of PH [40, 43].

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