DIRECT AND SENSITIZED *SYN–ANTI* PHOTOISOMERIZATION OF BENZOYLPYRIDINE-4-NITROPHENYLHYDRAZONES

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Summary

syn–anti Photoisomerization of 2-benzoylpyridine-4-nitrophenylhydrazone(I) and 3-benzoylpyridine-4-nitrophenylhydrazone(II) by direct excitation and by benzophenone sensitization has been investigated. Under direct irradiation the *syn* form of I undergoes irreversible isomerization to the *anti* form, whereas compound II attains a photo-equilibrium state of the *syn–anti* isomers. The different behaviour of the two compounds has been attributed to a hydrogen bond between the NH group and the pyridine nitrogen in the singlet excited state of *anti* I, this latter state being responsible for the direct photoisomerization. As the sensitization involves the triplet states, which are not affected by the hydrogen bond, it brings about a photo-equilibrium state of *syn–anti* isomers for both compounds studied.

1. Introduction

Photoisomerization studies of most imines are complicated by the low thermal barrier between the two isomers. Because of this barrier the photochemically induced shift in the isomeric equilibrium is frequently followed by rapid thermal relaxation which re-establishes the initial configurational equilibrium [1, 2]. However, in the hydrazone derivatives of aromatic aldehydes and ketones the thermal barrier is high enough so as to prevent thermal interconversion. This feature allowed us to prepare by irradiation and to isolate by chromatography some stable *syn* and *anti* isomers of hydrazones of aromatic aldehydes [3, 4].

Our earlier investigations [5 - 8] have shown that the path of the photoisomerization about the C=N group is remarkably sensitive to the groups attached to the double bound and to their substituents. It was found that in some phenylhydrazones the direct photoisomerization involves the lower trip-

let excited states, while in the 4-nitrosubstituted analogues the more probable mechanism rules out these states. Clearly further experimental findings would be required to complete the understanding of the mechanism of the photoisomerization about the C=N group, and with this purpose we carried out the present work dealing with the direct and sensitized photoisomerization of 4-nitrophenylhydrazones of 2- and 3-benzolpyridine.

2. Experimental

2.1. Materials

2-Benzoylpyridine-4-nitrophenylhydrazóne (I) and 3-benzoylpyridine-4-nitrophenylhydrazone (II) were prepared by refluxing an ethanolic 4-nitrophenylhydrazone solution with an equimolecular quantity of benzoylpyridine for 2 h. A mixture of *syn* and *anti* forms of I and II was obtained (Scheme 1).

| syn I | anti I | syn II | anti II |
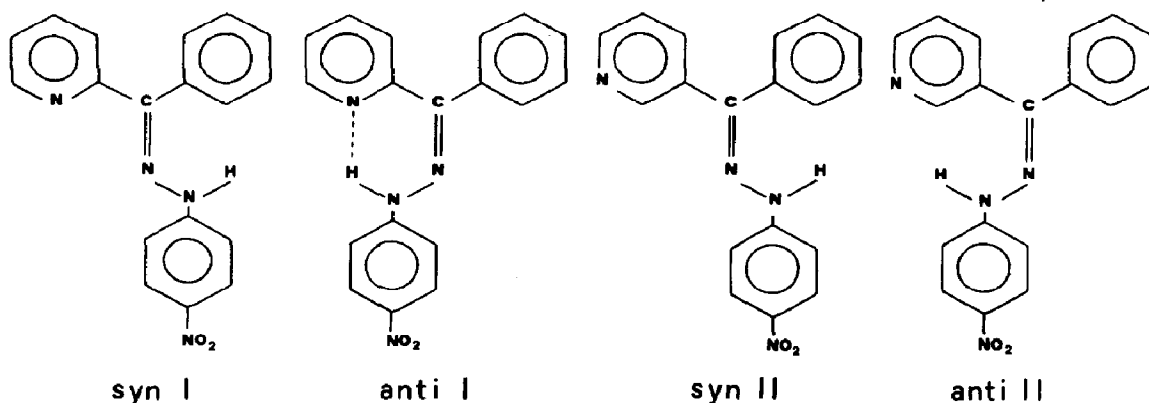
Scheme 1.

The *syn* and *anti* isomers were isolated using a silica gel column by altering the eluent from benzene to ethyl acetate and they were recrystallized from ethanol. The purity of the products was tested by thin layer chromatography and elementary analysis. The melting points are: *syn* I 175 - 176 °C; *anti* I 204 - 205 °C; *syn* II 217 - 218 °C; *anti* II 197 - 198 °C. The compounds are stable in the dark and under a nitrogen atmosphere.

The configurations of the two geometric isomers of compound I can be assigned easily because in the *anti* form there is an intramolecular hydrogen bond between NH group and the pyridine nitrogen. The nuclear magnetic resonance (NMR) spectrum of the *anti* form shows a signal at δ 14 due to the nitrogen-linked proton which is not observable in the spectrum of the *syn* form. In the IR spectra the shift of the NH stretching vibration and the alteration of the pyridine ring vibrations [9] provide further evidence regarding relative configurations of both forms. Finally in the UV spectra the first band $\pi-\pi^*$ shifts to higher wavelengths in the *anti* isomer (in benzene *syn* I: $\lambda_{max} = 390$ nm, $\epsilon_{max} = 41\ 000$; *anti* I: $\lambda_{max} = 415$ nm, $\epsilon_{max} =$

45 300); this shift can be accounted for if we consider that the hydrogen bond leads to the formation of a planar ring in conjugation with the aromatic system.

For the isomers of compound II the configurational assignment is complicated because there are no significant differences between their NMR and UV spectra (in benzene *syn* II: λ_{max} = 387.5 nm, ϵ_{max} = 37 000; *anti* II: λ_{max} = 387.5, ϵ_{max} = 40 500). Only the IR spectra in CCl_4 show any suitable differences, which provide indications for two relative configurations. In the *syn* isomer the stretching vibration of the NH group lies at the same frequency as that observed in *syn* I. In the *anti* isomer the frequencies of the stretching of NH and of the bending of the pyridine ring shift to higher energy (respectively from 3300 to 3350 and from 680 to 700 cm^{-1}). These shifts point to a reciprocal hindrance of the two groups, as expected in the *anti* configuration.

Benzophenone (Baker) and dicyclopentadienyliron (Baker) were suitable for "sensitizer use". Benzene was of spectroscopic grade. All reagents were analysis pure.

2.2. Apparatus and procedures

The experimental equipment for irradiation, for measurements of the incident light and for spectra were the same as described previously [8]. We used radiation of wavelengths 313, 333, 365 and 405 nm. The intensity of the light was of the order of 10^{-7} - 10^{-8} $Nh\nu$ min^{-1}. In the direct isomerization experiments benzene solutions of pure isomers in the concentration range 10^{-5} - 10^{-3} M for compound I and 10^{-4} - 10^{-3} M for compound II were irradiated in standard spectrophotometric cells. The photochemical reaction was considered to be a *syn–anti* isomerization because (a) the absorption spectra of an irradiated solution fitted that of a mixture of *syn–anti* isomers of concentration equal to that of the initial isomer and (b) chromatographic separation of the irradiated solution yielded the *syn* and *anti* isomers. The quantum yields were calculated from the initial rate for solutions that completely absorb the incident light (optical density higher than 2) and by Zimmerman's [10] method for solutions of lower optical density.

In the experiments employing sensitized benzophenone isomerization, samples of concentration of the order 10^{-4} M and benzophenone of about 0.12 M were irradiated at 333 nm and the reaction was followed spectro-photometrically at a wavelength greater than 410 nm, a region in which the absorption of the sensitizer is negligible. The experiments were carried out in spectrophotometric cells sealed after deoxygenation. The quantum yields were calculated from the initial rate of the reaction; we considered the direct isomerization due to the absorption of the sensitizer phosphorescence to be negligible.

The fluorescence spectra of compounds I and II (at about 10^{-5} M) were observed by excitation at 365 nm. The fluorescence quantum yields were determined relative to that of quinine sulphate in 0.1 N H_2SO_4 using the

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TABLE 1

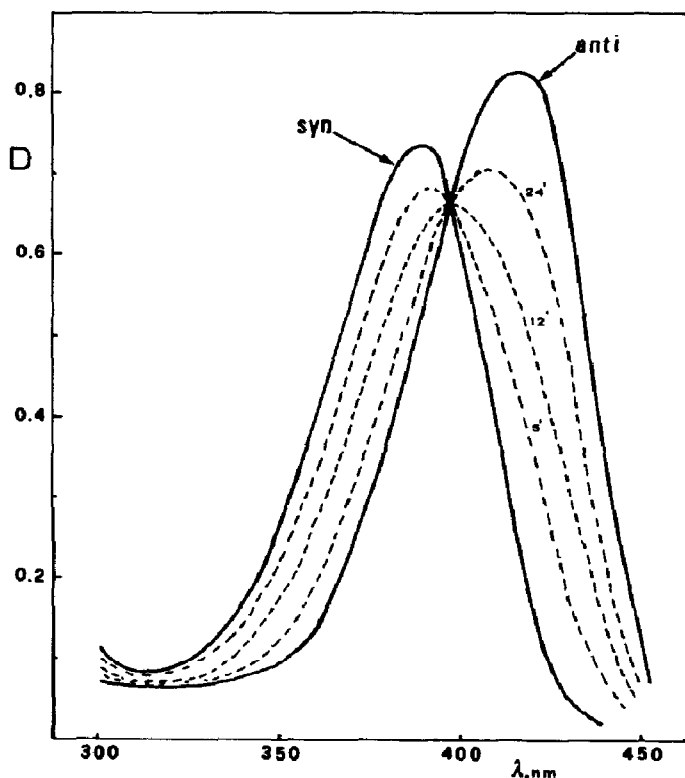|	*syn* I	*anti* I	*syn* II	*anti* II
λ_{Fmax} (nm)	448	458	450	450
Φ_F	0.6×10^{-3}	$<10^{-4}$	0.9×10^{-3}	0.9×10^{-3}

Fig. 1. Spectral changes after photoisomerization of *syn*I in benzene under 365 nm irradiation. The numbers on the curves give the irradiation time in minutes.

suitable formula [11]. For *anti* I the values of the fluorescence intensity were corrected for the inner filter effect.

3. Results

The absorption spectra of I and II show the characteristic band at about 390 nm [5]. No n–π* bands are observable probably because they are overlapped by the intense π–π* band. Some attempts carried out in the presence of C_2H_5I did not reveal any intensity that could be assigned to absorption from the ground to the triplet state.

All the isomers show fluorescence emission. The values of the wavelengths at maxima λ_{Fmax} and of the quantum yields ϕ_F (the latter with an error of 15%) are reported in Table 1. From the fluorescence spectra it is possible to calculate the energy of the S_1 state to be about 63 kcal.

No phosphorescence of the compounds was observed at 77 K in methylcyclohexane–isopentane solutions and we have thus not been able to estimate the energy of the T_1 state.

3.1. Direct photoisomerization

Under direct irradiation *syn* I and both the isomers of compound II undergo *syn–anti* isomerization. The quantum yields were independent of the initial concentrations and of the exciting light wavelengths.

For compound I the *syn–anti* conversion is complete (Fig. 1) at all irradiation wavelengths because the *anti* isomer is photochemically inactive. The average value of the quantum yield ϕ_{s-a} is 0.30 ± 0.01.

For compound II reversible *syn–anti* photoisomerization occurs with quantum yields of $\phi_{a-s} = 0.25 \pm 0.02$ and $\phi_{s-a} = 0.22 \pm 0.02$. At all wavelengths the photoequilibrium state is close to that predicted by the relation

$$\frac{\Phi_{s-a}}{\Phi_{a-s}} = \frac{\epsilon_a[\text{anti}]_e}{\epsilon_s[\text{syn}]_e}$$

3.2. Quencher and temperature effect

In order to detect a possible triplet state in the reaction some photochemical kinetics were followed with solutions of I (or II) containing the substrate at a suitable concentration (10^{-3} - 10^{-4} M) and dicyclopentadienyl-iron (10^{-2} M) which were irradiated at 365 nm. After allowing for quencher absorption, it was found that the quantum yields are not influenced by the quencher.

Experiments carried out with non-deaerated solutions provide the same quantum yield values as those with deaerated ones.

Lastly other experiments indicated that the temperature in the range 25 - 50 °C does not affect the photochemical kinetics.

3.3. Sensitized photoisomerization

Reversible photoisomerization of both compounds can be induced by benzophenone ($E_T = 69$ cal). The results show that the apparent initial quantum yields of the photoisomerization increase with the concentration of compounds I or II. Plots of $1/\phi_{app}$ versus $1/[\text{compound}]$ (Fig. 2) give good straight lines, from whose intercepts the limiting quantum yields were calculated using the relation

$$\frac{1}{\phi_{app}} = \frac{1}{\Phi_{lim}} \left(1 + \frac{1}{k_s \tau [\text{compound}]} \right)$$

For compound I $\Phi_{s-a} = 0.58$ and $\Phi_{a-s} = 0.37$; for compound II $\Phi_{a-s} = 0.26$ and $\Phi_{s-a} = 0.28$. The ratios of the intercepts to the slopes give the sensitization
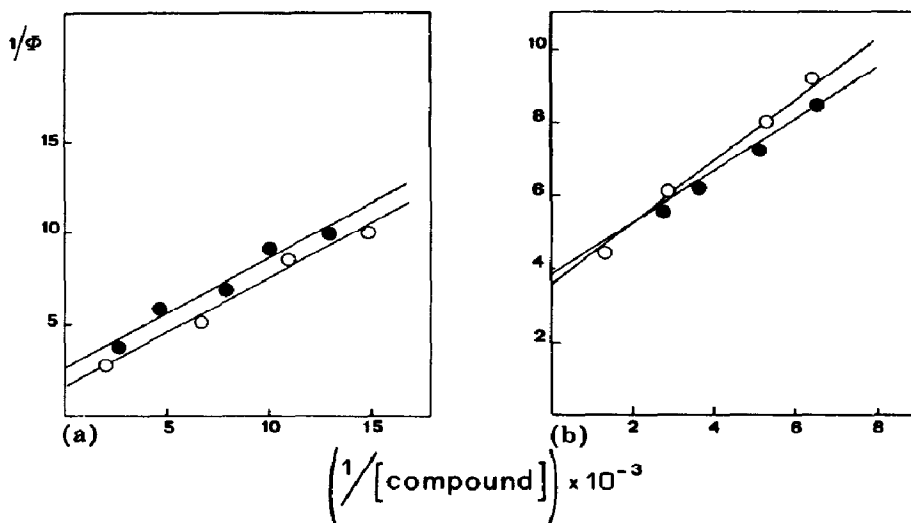
Fig. 2. The isomerization of the compounds I (a) and II (b) photosensitized by benzophenone: O, syn → anti; ●, anti → syn.

constants τk_s, where the lifetime τ of benzophenone is 1.9×10^{-6}. The values found for k_s are $2.5 \times 10^9 \, M^{-1} \, s^{-1}$ for *anti* I and $1.8 \times 10^9 \, M^{-1} \, s^{-1}$ for *syn* I and for both the isomers of II. These values are near to that predicted for a diffusion-controlled process. This shows that benzophenone behaves as a high energy sensitizer for the compounds studied.

4. Discussion

The following conclusions can be made about the isomerization mechanism of compounds I and II. For compound I the absence of photochemical reactivity and the quenching of fluorescence in the *anti* isomer can be attributed to the hydrogen bond present in the ground and excited singlet states. In fact it is known [12, 13] that when a hydrogen bond connects two π systems there is an increase in the rate of internal conversion and the resultant shortening of the excited singlet lifetime quenches the photoreactivity and fluorescence yields, as was found in the present case. This implies that the excited molecule decays to the ground state without having the possibility of attaining the excited state in which the photoisomerization takes place. The inefficiency encountered with the quenching experiments indicates almost no involvement of triplet states in the direct photoisomerization. Therefore, according to these considerations, the photoisomerization process must involve an electronically excited singlet state. Two pathways are possible. (a) The rotation of the azomethinic bond in the lower excited singlet state $^1syn^*$ leads to a common twisted singlet state ^1p attainable only from the *syn* isomer. The twisted configuration could repre-

sent the minimum in the potential surface energy of the excited singlet states, from which the molecule decays to the *syn* and *anti* forms in the ratio of $\alpha/(1-\alpha)$:

$$syn + h\nu \rightarrow {}^1syn* \qquad (1)$$

$$^1syn* \rightarrow syn + h\nu' \qquad (2)$$

$$^1syn* \rightarrow syn \qquad (3)$$

$$^1syn* \rightarrow {}^1p \qquad (4)$$

$$^1p \rightarrow \alpha syn + (1-\alpha)anti \qquad (5)$$

$$anti + h\nu \rightarrow {}^1anti* \qquad (6)$$

$$^1anti* \rightarrow anti \qquad (7)$$

(b) An alternative pathway could involve a *syn* → *anti* conversion which could take place by a normal thermal process on the potential energy surface through a barrier separating the two configurations:

$$syn \underset{}{\overset{h\nu}{\rightleftharpoons}} {}^1syn* \rightarrow {}^1anti* \underset{h\nu}{\overset{}{\rightleftharpoons}} anti$$
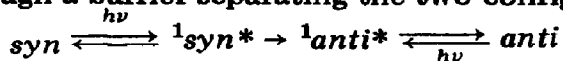
However, the observed invariability of the quantum yields with temperature suggests that no thermally activated step occurs in the isomerization process and so we prefer pathway (a). Also the short lifetime of $^1syn*$ (about 10^{-11} - 10^{-12} from Φ_F data and from the radiative lifetime calculated from absorption spectra) confirms our preference.

The non-participation of the triplet states in the process of photo-isomerization is attributable to the lack of intersystem crossing between singlet and triplet states. In fact when these triplet states are populated by energy transfer compound I undergoes a *syn* ⇄ *anti* isomerization. It is possible for this reversible reaction to occur since the hydrogen bond does not affect these states. The data obtained regarding the quantum yields ($\Sigma\Phi$ → 1) and the photoequilibrium state

$$\frac{\Phi_a}{\Phi_s} = \frac{[syn]_e}{[anti]_e}$$

can be interpreted using a classical scheme [14] in which a twisted state ^3p which is populated either by energy transfer or by decay from the originally populated triplet states decays to the *syn* and *anti* forms in the ratio of $\beta/(1-\beta)$:

$$^3S* + syn \rightarrow S + {}^3syn* \qquad (8)$$

$$^3S* + anti \rightarrow S + {}^3anti* \qquad (9)$$

$$^3syn* \rightarrow {}^3p \qquad (10)$$

$$^3anti* \rightarrow {}^3p \qquad (11)$$

$$^3p \rightarrow \beta syn + (1-\beta)anti \qquad (12)$$
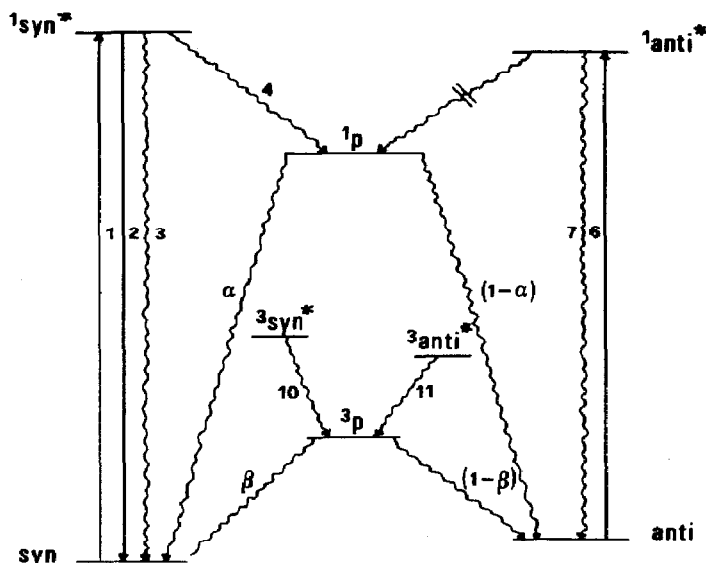
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Fig. 3. The schematic mechanism for the direct and sensitized photoisomerization of compound I.

In conclusion the approximate scheme given in Fig. 3 summarizes the proposed mechanism for the direct and sensitized isomerization of compound I.

If the implications arising from the hydrogen bond are ruled out, the photochemical behaviour of compound II is strictly comparable with that of I, so that a similar scheme can be used to interpret the relative results. The most important difference consists in the fact that the state ^1p is attained from both $^1syn*$ and $^1anti*$ configurations. Then from the ^1p state, in the case of direct reaction, or from the state ^3p, in the case of sensitized reaction, the molecule can decay to two geometric forms with almost the same probability, as is suggested by the proximity of the quantum yield values. Another possibility of direct photoisomerization of I and II may be considered. If the source of the inefficiency of the quencher is related to the lower triplet state energy of substrate or to its short lifetime, an alternative mechanism to that proposed for direct photoisomerization might involve a crossing between singlet and triplet pathways. The singlet twisted state ^1p could undergo intersystem crossing to ^3p, a common intermediate triplet state for direct and sensitized reaction, with an efficiency lower than unity ($\eta = 0.30/0.58$) for compound I and about unity for compound II. The closeness of the direct and sensitized quantum yield values, particularly in the case of compound II strongly supports the second hypothesis.

Acknowledgment

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