

THE PHOTOCHEMICAL ISOMERIZATION OF THE PYRIDINE-2-ALDEHYDE
4-NITROPHENYLHYDRAZONE

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syn-anti Photoisomerization of 4-nitrophenylhydrazone of pyridine-2-aldehyde by direct and benzophenone sensitized excitation has been investigated.

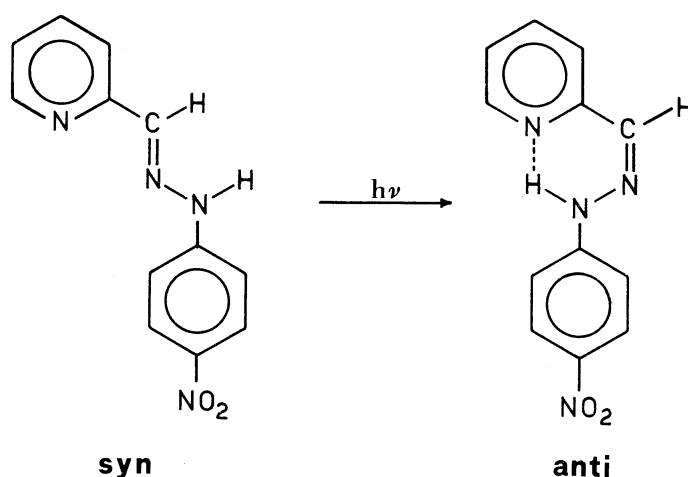
For direct irradiation, the *syn*-isomer undergoes complete isomerization to *anti*; for sensitized irradiation, a photoequilibrium state between two isomers is obtained.

Two different mechanisms are proposed.

Previously we have extensively investigated the substituent effects on the kinetics of direct and sensitized photoisomerization of phenylhydrazones^{1,4}. The interesting results obtained have led us to extend the investigations to analogous systems, in which a heteroatom has been introduced in the aldehyde skeleton; in this paper we report the results of a study of the photochemical behaviour of the 4-nitrophenylhydrazone of pyridine-2-aldehyde.

syn-Pyridine-2-aldehyde 4-nitrophenylhydrazone is prepared by classic methods and recrystallized by ethanol (m.p. 274-5 °C).

During irradiation of solutions of this compound *syn-anti* irreversible isomerization occurs



At all wavelengths, the final state is the same and it is constituted by pure *anti*-isomer. This latter, therefore, is prepared by irradiating concentrated solution of *syn*-isomer in benzene until complete isomerization. This *anti*-isomer is then precipitated by adding cyclohexane and then recrystallized by ethanol. The purity of the product is tested by thin layer chromatography, elementary analysis and constant melting point (183°C). The UV spectra of the two isomers are shown in Table 1.

Table 1. Ultraviolet absorption maxima for the pyridine-2-aldehyde 4-nitrophenylhydrazone.

<i>syn</i>		<i>anti</i>	
λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	$\log \epsilon$
Benzene			
385	4.572	405	4.618
(330)	3.740		
300	3.726	305	3.568
Chloroform			
390	4.578	410	4.627
(330)	3.820	(325)	3.574
300	3.820	295	3.567

region the first π, π^* band, which is more intense than in the analogous phenylhydrazones, because of the auxochrome effect of the nitro group. The red shift of the π, π^* band of the *anti*-isomer, compared to that of the *syn*-isomer, indicates the existence of an intramolecular hydrogen bond between the nitrogen atoms of the pyridine ring and the anilino group. A

planar six membered ring is formed in conjugation with the aromatic systems.

Besides, in the IR spectra, the shift of the NH stretching vibration and the alteration of the pyridine ring vibrations provide further evidence regarding relative configurations of two isomers and the existence of the hydrogen bond.

For the kinetics of the direct isomerization, experiments were carried out by irradiating benzene and chloroform solutions of hydrazone in concentration of about 10^{-5} M, deoxygenated by bubbling with pure nitrogen. The radiations used *viz.* 405, 365, 333 and 313 nm were isolated from a Hg lamp (Hanau Q 400) by means of interference filters (Schott and Co.). The reaction was followed spectrophotometrically at 410 nm (fig.1). The quantum yields, calculated by Zimmerman's method⁵, are shown in Table 2.

It is interesting to note that generally the quantum yields decrease with the energy of the exciting radiation, independently of the nature of the corresponding absorption band. This suggests that the reactions leading to the isomerization occur more rapidly than the vibrational relaxations, and rules out the possibility of a common intermediate state in the mechanism. The low value found at 313 nm can

be due to a side decomposition provoked by the photon energy.

Table 2. Quantum yields for *syn*→*anti* direct photoisomerization. Temp. 25° C.

Solvent	λ_{exc} (nm)			
	313	333	365	405
Benzene	0.407 ± 0.004	0.503 ± 0.005	0.364 ± 0.004	0.340 ± 0.004
Chloroform	0.262 ± 0.003	0.308 ± 0.002	0.225 ± 0.005	0.117 ± 0.004

On comparison with the corresponding phenylhydrazone⁶, the introduction of the nitro group in the N-aryl ring increases the *syn*→*anti* isomerization quantum yields, as observed in analogous systems⁴, but lessens the quantum yields of *anti*→*syn* to zero. The lack of the photosensitivity in the *anti*-isomer proves that the hydrogen bond in the ground and in the excited state is reinforced by the nitro group, so

that the configuration variation, involving the breaking of this bond, is prevented.

The usual solvent-solute interaction is responsible for the observed effect on the quantum yields.

Sensitized photoisomerization can be induced by benzophenone ($E_T=69$ Kcal mole⁻¹). Preliminary experiments, regarding quenching of sensitizer phosphorescence by *syn*-isomer, demonstrate that there is efficient triplet transfer, controlled by diffusion ($K_q=0.9 \times 10^{-9}$ mole⁻¹ sec.⁻¹). The test cannot be carried out with the *anti*-isomer, because of the fluorescence of the latter.

For the kinetics of sensitized photoisomerization, mixtures of substrate (10^{-5} M) and benzophenone (0.25 M) were irradiated at 333 nm; in these experimental conditions the light can be considered entirely absorbed by the sensitizer.

Contrary to what was observed in the direct reaction, the sensitization leads to a photostationary state, achieved by both isomers, of constant composition: $[anti]_s = 68\%$; $[syn]_s = 32\%$.

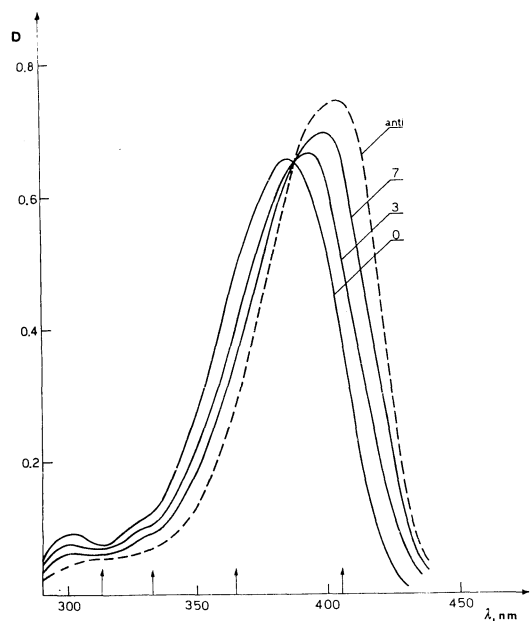


Fig.1. Spectral changes of a cyclohexane solution of the pyridine-2-aldehyde 4-nitrophenylhydrazone under 405 nm irradiation. Numbers refer to time in minutes. The arrows refer the wavelengths of the exciting radiation.

The quantum yields $\Phi_{s \rightarrow a}$, calculated by the Lamola-Hammond formula⁷, increase with the concentration of the acceptor. The plot of $1/\Phi_{s \rightarrow a}$ vs. $1/[\text{syn}]$ is a good straight line; from the extrapolation to $1/[\text{syn}] = 0$, the limiting value of the quantum yield $\Phi_{s \rightarrow a} = 0.342$ is obtained. The ratio of the intercept to slope gives the sensitization constant, from which a value of K_q of the order 10^{-9} is obtained.

The rate of the *anti* \rightarrow *syn* isomerization is too low; therefore these quantum yields are calculated by the initial rate. This decrease with the substrate concentration and the extrapolation of plot $1/\Phi_{a \rightarrow s}$ vs. $1/[\text{anti}]$ leads to the limiting value, $\Phi_{a \rightarrow s} = 0.004$. This value is very much lower than that predicted (0.16) by the photostationary state composition and this suggests that the *anti*-isomer is the poorer acceptor of the pair. The source of the inefficiency can be related to the fact that, because of the hydrogen bond, the *anti*-isomer has a rigid structure and the energy transfer that would bring about a change in geometry would be highly prejudiced. The composition of the stationary state is determined by the decay ratio of the common triplet intermediate, attainable from either isomer.

By comparison of the results of the direct and sensitized reaction, it is thought that the two processes occur by different paths; in the case of direct photoisomerization, the reaction possibly occurs during or immediately after the decay of the excited molecule in vibrationally excited levels of the ground state, such as a thermal reaction, without crossing to the triplet state.

As a final comment, we wish to point out that the most important effect of the introduction of the heteroatom arises from the formation of the hydrogen bond.

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