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Short Communication

Mechanism of direct photoisomerization of pyridylhydrazones

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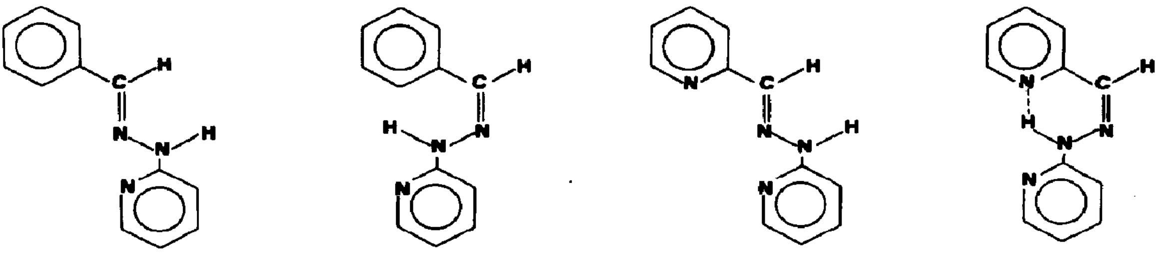
1. *Introduction*

Previous photochemical investigations of hydrazones [1 - 4] have shown that both direct excitation and triplet energy transfer are effective in bringing about *syn–anti* isomerization. A less certain aspect of the reaction mechanism is whether the direct photolysis leads to isomerization via the singlet manifold or whether intersystem crossing precedes isomerization. This uncertainty has arisen because the results seem to lead to different conclusions according to the particular compound investigated. Further experimental findings are therefore necessary to clarify this problem; with this purpose we carried out an investigation of the direct photoisomerization of benzaldehyde-2-pyridylhydrazone (I) and pyridine-2-aldehyde-2-pyridylhydrazone (II) (see Fig. 1). In addition, some supplementary information about the effect of substituting the phenyl ring with the pyridine ring was obtained which allowed us to make further observations about the influence of hydrogen bonding.



syn I anti I syn II anti II

Fig. 1. The structures of the compounds investigated.

2. *Experimental*

2.1. *Materials*

Syn-Benzaldehyde-2-pyridylhydrazone (*syn* I) and *syn*-pyridine-2-aldehyde-2-pyridylhydrazone (*syn* II) were prepared by classic methods and were recrystallized from ethanol. (The melting points are 151 - 152 °C and 181 - 182 °C respectively). The *anti* isomers were prepared by irradiating concentrated benzene solutions and were isolated by thin layer chromatography using as eluents an ethyl ether–petroleum ether mixture (40:60) for *anti*-benzaldehyde-2-pyridylhydrazone (*anti* I) and an ethyl acetate–ethyl ether mixture (40:60) for *anti*-pyridine-2-aldehyde-2-pyridylhydrazone (*anti* II) (m.p. 67 - 68 °C). The *anti* I isomer was obtained only in solution.

In the IR spectra the shift of the NH stretching vibration and the alteration of the pyridine ring vibrations provide evidence for the *syn* and *anti* configurations and for the hydrogen bond in the *anti* II form [5]. In the UV spectra the shift of the $\pi-\pi^*$ band in benzene solution further confirms the geometric configurations and the presence of the hydrogen bond (*syn* I: $\lambda_{max} = 327.5$ nm, $\epsilon_{max} = 27\,700$; *anti* I: $\lambda_{max} = 307.5$ nm, $\epsilon_{max} = 16\,750$; *syn* II: $\lambda_{max} = 331$ nm, $\epsilon_{max} = 29\,550$; *anti* II: $\lambda_{max} = 356.5$ nm, $\epsilon_{max} = 23\,100$). All other chemicals were reagent grade.

2.2. *Apparatus and procedures*

The experimental equipment for irradiation, for measurements of the incident light and for spectra were the same as those described previously [6].

Benzene solutions of pure isomers in the concentration range 10^{-3} - 10^{-5} M were irradiated at 313, 333 and 365 nm in standard spectrophotometric cells after deaeration with nitrogen. The kinetics of the photoreaction were followed in a suitable region of the absorption. The constant isosbestic points and the chromatographic analysis indicated that only one product was formed by irradiation and no side reactions could be detected. In the experiments carried out with quenchers and heavy atoms, the relative concentrations of substrate and of quenchers or heavy atoms were such that the irradiation was almost completely absorbed by the substrate.

3. *Results and discussion*

Under direct irradiation compound I underwent *syn*$\rightleftarrows$*anti* isomerization (Fig. 2(a)) and the photostationary state attained from the *syn* isomer was the same as that attained from the *anti* isomer. No side reactions were detectable. Under the same conditions compound II (Fig. 2(b)) underwent *syn* → *anti* isomerization until complete conversion. The quantum yields were independent of the initial concentration and of the irradiating wavelengths of 365, 333 and 313 nm. The following values were obtained: for I $\Phi_{s-a} = 0.1 \pm 0.007$ and $\Phi_{a-s} = 0.23 \pm 0.015$; for II $\Phi_{s-a} = 0.07 \pm 0.005$.

The fact that the quantum yield values are the same supports the hypothesis that the reaction arises from one excited intermediate state which can be singlet or triplet. In order to make this singlet–triplet distinction we

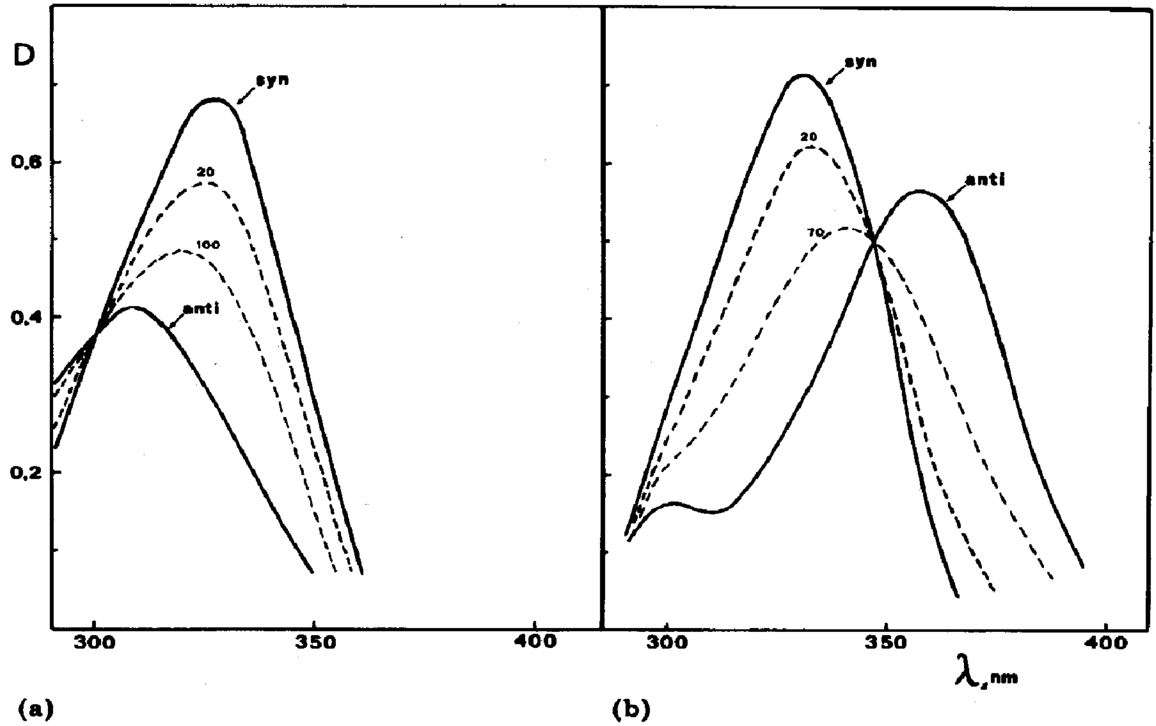


Fig. 2. Spectral changes after photoisomerization of (a) *syn* I and (b) *syn* II in benzene under 333 nm irradiation. The numbers on the curves give the irradiation time in minutes.

carried out experiments based on the quenching of the excited electronic states and on the heavy atom effect. A preliminary study has dealt with the problem of approximately determining the energy of the triplet state. Since the hydrazones under consideration neither phosphoresce nor reveal, in the presence of heavy atoms (xenon or C_2H_5I), any absorption intensity which can be assigned to absorption from the triplet state, we have performed preliminary sensitization experiments which indicate that the triplet energy of the *syn* isomers is greater than 40 kcal. Consequently ferrocene and azulene are suitable quenchers of the isomerization. It is not convenient to use oxygen as a quencher because some side oxidation reactions can occur. The irradiation of solutions of I and II containing ferrocene or azulene leads to photoisomerization with the same quantum yields as those found by irradiating the substrate solutions alone; therefore these quenchers do not affect the photoreaction. Since the observed inefficiency could arise because the excited states do not have a sufficiently long lifetime to be intercepted, the effect of heavy atoms on possible singlet–triplet intersystem crossing was examined. Experiments were carried out in benzene solutions saturated with xenon and in acetonitrile solutions containing 10^{-2} M NEt_4Br. The results show clearly that the heavy atom does not affect the photoisomerization process. Attempts to carry out investigations in bromobenzene in order to observe possible heavy atom effects were unsuccessful; in fact under these conditions the quantum yields decreased drastically because of the solvent polarity, as has also been found in analogous compounds [1, 7]. In a series of experiments both heavy atoms and quenchers were used to ensure that the absence of an effect was not the result of almost equal quantum yields from the singlet and triplet states; the inefficiency of both perturbers ruled out this possibility.

The overall results show clearly that neither the heavy atoms nor the quenchers have any effect on the direct photoisomerization process and also show that its pathway bypasses the triplet state. The more probable mechanism, which agrees with the results obtained, can be described by the following model. The molecule, excited to the lowest singlet state, undergoes rapid relaxation to the minimum of the potential energy surface, with concomitant twisting or nitrogen inversion, where it acquires an intermediate geometry between the *syn* and *anti* configurations. From this minimum point a decay occurs to the ground *syn* and *anti* states. Because the sum of the quantum yields Φ_{s-a} and Φ_{a-s} is less than unity, deactivation of the singlet state must also include other important radiationless decay processes which occur with geometric configuration retention. Indeed, these latter paths must be the only deactivation route for the excited molecule of *anti* II. In this compound, as has been found previously in analogous compounds [4], the hydrogen bond, present in both the ground and excited states, increases the internal conversion rate by decay processes; however, the molecule of *anti* II retains its original configuration. In the proposed model we consider that, in the compounds studied, all radiationless decays are too rapid for intersystem crossing to be a competitive deactivation path; this conclusion is supported by the lack of phosphorescence.

With respect to the nature of the intermediate geometry in the singlet state minimum, the data do not provide any indication of a relaxation occurring through inversion or rotation. However, making use of the fact that the quantum yields of the two pyridylhydrazones are of the same order as those found for analogous phenylhydrazones [1], some deductions are possible. The observed insensibility to aza substitution suggests that, in both the pyridine and phenyl compounds, the same mechanism is operative in the direct photoisomerization. In previous investigations of the substituent effects in the thermal and photochemical isomerizations of phenylhydrazones [1, 8] we concluded that the photoisomerization involves torsional motion, in contrast with the thermal isomerization which occurs through lateral shift. By extending these conclusions to the pyridylhydrazones studied in this work, we believe that it is reasonable to suggest that the relaxation to the minimum of the lowest excited singlet state proceeds via torsion.

1 G. Condorelli, L. L. Costanzo, S. Pistarà and S. Giuffrida, *Z. Phys. Chem., N. F., 90* (1974) 58.
2 G. Condorelli, L. L. Costanzo, S. Giuffrida and S. Pistarà, *Z. Phys. Chem. N. F., 96* (1975) 97.

3 G. Condorelli, L. L. Costanzo, L. Alicata and A. Giuffrida, *Chem. Lett. (Chem. Soc. Jpn.)*, (1975) 227.
4 L. L. Costanzo, S. Giuffrida, U. Chiacchio and G. Condorelli, *J. Photochem.*, *11* (1979) 39.
5 N. Colthup, L. Daly and S. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964.
6 L. L. Costanzo, S. Pistarà, G. Condorelli and G. Scarlata, *J. Photochem.*, *7* (1977) 297.
7 G. Condorelli, L. L. Costanzo, S. Giuffrida and S. Pistarà, *Boll. Accad. Gioenia (Catania) Serie IV, XII* (1974) 531.
8 G. Condorelli and L. L. Costanzo, *Boll. Accad. Gioenia (Catania) Serie IV, VIII* (1966) 775.