## Photochemistry of arylhydrazides in solution

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The photochemical reactions of arylhydrazides ArCONHN=CHR in solution were studied. The main photochemical process was shown to be *trans-cis* isomerization with a quantum yield of 0.2-0.8 and an activation energy of 21-24 kcal mol<sup>-1</sup>.

**Key words:** photochemical reactions, arylhydrazides, quantum yield, *trans-cis* isomerization, luminescence, activation energy.

Photochemical transformations of aromatic compounds containing the C=N double bond were studied by many authors. Their photochemical properties have been described in reviews and monographs.<sup>1-3</sup> The main photoreaction of arylazomethines is the *trans*—*cis* isomerization (or E-Z isomerization) relative to the C=N double bond; however, the presence of protondonating and proton-withdrawing groups (OH, CO) in the molecule can result in intramolecular hydrogen transfer or rearrangement of the whole molecule. In this work, we studied the photochemical reactions of arylhydrazides (1-5) in solution.

$$R^{1} R^{2} R^{3}$$

$$R^{1} Ph Ph H$$

$$Ph Ph Ph$$

$$R^{1} R^{3} Ph$$

$$H R^{2}$$

$$R^{3} Ph$$

$$H R^{2} Ph Ph Ph$$

$$R^{3} Ph$$

$$R^{2} Ph Ph Ph$$

$$R^{3} Ph$$

$$R$$

Arylhydrazides 1-5 differ from other classes of azomethines by the presence of the carbonyl group. One of the main photochemical reactions in carbonyl-containing aromatic compounds, for example, aromatic ketones, is photoreduction, which may appear for arylhydrazides.

## Experimental

Arylhydrazides 1 and 3-5 were synthesized from the hydrazides of acids and the corresponding aldehydes by heating for 0.5 h in anhydrous EtOH on a water bath. Compound 2 was prepared from equimolar amounts of benzophenone and benzhydrazide by heating for 8 h in a sealed tube at 120 °C. The melting points of samples 1-5 are presented in Table 1.

Absorption spectra were recorded on a Specord M-40 instrument. Irradiation was carried out using DRSh-1000 and DKSSh-100 lamps with a Hitachi G-3 monochromator. Fluorescence spectra were studied with homemade equipment described previously.<sup>4</sup> The quantum yield of isomerization ( $\varphi_{t-c}$ ) was determined relative to  $\varphi_{t-c} = 0.5$  for stilbene isomerization in EtOH.

Main measurements were performed in EtOH solutions at room temperature, and in some cases, absorption and luminescence spectra were studied at 77 K.

## **Results and Discussion**

The spectral and photochemical properties of arylhydrazides 1-5 are presented in Table 1. The absorption spectra of arylhydrazides in solution (Fig. 1) resemble those of arylazomethines with the general structure  $Ar^1-HC=N-Ar^2$ , 1.5 for which the absorption is explained by transitions between the  $\pi$ -orbitals of two chromophores. One chromophore contains the whole

Com- pound	M.p./°C	$\frac{\lambda_{max}}{(cm^{-1})}$	ε /L mol <sup>-1</sup> s <sup>-1</sup>	φ <sub>r-c</sub> (310 nm) ±0.05	φ <sub>c-1</sub> (405 nm) ±0.05	E <sub>a</sub> /kcal mol <sup>-1</sup>
1	210	33000	31000	0.32	≲0.1	21.6
2	116	33500	25000			
3*	207	31500	28000	0.75	0.12	22.2
4	250	34500	25000	0.2		22.5
5	187	30500	25000	0.22		23.7

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Fig. 1. Absorption spectra of arylhydrazides 1-5 (*a-e*, respectively) in ethanol at 20 °C (*I*) and after UV irradiation at 313 nm for 30 s (2).

molecule whose  $\pi$ -orbital is designated as  $\pi_1$ , and in its basis set the N atom is represented by the  $p_1$ -orbital. The second chromophore contains only the amine part whose  $\pi$ -orbital is designated as  $\pi_2$ , and its basis set contains the  $p_2$ -orbital of the N atom. The  $\pi_2-\pi_1^*$  transition, *i.e.*, the transition of an electron from the  $\pi^*$ -orbital of the whole molecule, is responsible for the long-wave absorption band of these compounds. This electron transition weakens the C=N double bond and facilitates the *trans-cis* isomerization.

Irradiation of the ethanol solution of arvlhydrazides in the region of 310 nm results in a change in the absorption spectrum and the appearance of absorption in the region of 400 nm (see Fig. 1). The spectra return to the initial state due to the further irradiation of the solutions by light with  $\lambda = 405$  nm. The initial state of the spectrum can also be attained on prolonged storage of the solution in the dark. These photo- and thermal transformations are independent of the presence or absence of oxygen in the solvent and of the polarity of the solvent (alcohol, hexane). This suggests that the trans-cis isomerization is the main photoreaction for the substances under study (the designations anti-syn, E-Z isometization are sometimes used for azomethines). The photochemical behavior of the arylhydrazides in solutions is identical to those of stilbene and azobenzene: isomerization is the main photochemical process and occurs with a high efficiency: For compound 3, the quantum yield of *trans-cis* isomerization is higher than that for stilbene. For the arylhydrazides with the hydroxyl substituent in the *ortho*-position of the phenyl fragment, the quantum yield of *trans-cis* isomerization considerably decreases, which is likely due to the presence of the hydrogen bond between the OH group and the N atom of the C=N group. Note that no photoisomerization processes are observed in chlorine-containing solvents (CH2Cl2, CCl4), which can be explained by the quenching of the excitation in the chargetransfer complex thus formed.

Substance 2 undergoes no photochemical transformations in solution under UV irradiation (300-400 nm), which should be expected. Its luminescence spectrum at room temperature is a bell-shaped curve with a maximum at -455 nm.

The activation energy  $E_a$  of the dark *cis*—*trans* isomerization of the substances under study (see Table 1) is much lower than that of arylstilbenes (~40 kcal mol<sup>-1</sup>) but is close to the values for N-benzylidenaniline (16 kcal mol<sup>-1</sup>)<sup>6</sup> and diaryl hydrazones (24–26 kcal mol<sup>-1</sup>).<sup>3</sup>

The main peculiarity of the arylhydrazides is that the efficiency of *cis*—*trans* photoisomerization is much lower than that in the case of *trans*—*cis* photoisomerization (see Table 1), unlike diarylethylenes for which the efficiencies of both reactions are similar ( $\varphi_{c-t} \approx 0.3$ ). For compound 3, with the characteristic and intense absorption spectrum in the *cis*-form, we succeeded in measuring the concentration of the *cis*-form in the starting solution



**Fig. 2.** Absorption (1 and 2) and luminescence (3 and 4) spectra of hydrazide of 3 in ethanol at 77 K ( $\lambda_{exc} = 310$  nm) (curves 1 and 3) and after irradiation at 20 °C ( $\lambda = 313$  nm) and freezing to 77 K (2 and 4).

and estimating the difference in the enthalpies of formation as  $\Delta H = 3.5$  kcal mol<sup>-1</sup>.

We studied the luminescence properties of the arylhydrazides at 77 K (Fig. 2, Table 1). The luminescence spectrum of the starting sample has a structureless form upon excitation in the region of 250-350 nm. After irradiation of the sample with light with  $\lambda_{max} = 310$  nm at room temperature, i.e., after trans-cis isomerization and freezing to 77 K, the luminescence spectrum takes a shape with a well-resolved vibrational structure with maxima at 19700, 21000, 22500, and 24000 cm<sup>-1</sup>. This spectrum almost completely coincides with the phosphorescence spectrum of benzophenone,<sup>7</sup> for which the radiative transition from the triplet  $n\pi^*$ -level is responsible:  $E_{00} = 24100 \text{ cm}^{-1}$ ,  $\Delta v \approx 1700 \text{ cm}^{-1}$ . In the case of arylhydrazide 1, this luminescence is excited up to 400 nm, i.e., in the absorption band of the cis-form. It can be assumed that in the *cis*-form the  $\pi_1 - \pi_1^*$  or  $\pi_2 - \pi_1^*$ transition is responsible for the absorption in the longwave band, and the emission occurs from the  $T_{n\pi^*}$  level of the amine part of the molecule, which is close in its properties to the benzophenone molecule. The strong intersystem crossing for the lowest singlet  $S_{\pi\pi^*}$  level to the triplet  $T_{n\pi^*}$  level occurs with the constant  $K_{ic} \approx 10^{10} \text{ s}^{-1}$ 

due to high spin-orbital coupling, and the emission occurs from the triplet level; the phosphorescence life-time being  $10^{-2}-10^{-3}$  s.

Similar results were obtained for compound 3: the emission spectrum of the *cis*-form corresponds to the phosphorescence of benzophenone. The low quantum yield of *cis*—*trans* photoisomerization of arylhydrazides 1 and 3 can also be explained by the fact that the excitation is localized on the ketone fragment of the molecule.

Compounds 4 and 5 differ from compounds 1 and 3 in luminescence properties: during *trans--cis* isomerization the shape of the luminescence spectrum remains unchanged, and only the emission intensity decreases. It can be assumed that states of the  $\pi\pi^*$ -type are the lowest excited states of the *cis*-isomers of 4 and 5, and the strong intramolecular hydrogen bond quenches the luminescence.

Thus, for the series of the arylhydrazides, the main photochemical process in solution is the *trans*cis (E-Z) isomerization, which occurs with a high quantum yield of 0.2-0.8. The activation energy of the dark cis-trans transition is 21-24 kcal mol<sup>-1</sup> (90-100 kJ mol<sup>-1</sup>).

## References

- V. A. Izmail'skii and Yu. A. Fedorov, in Azometiny [Azomethines, Collection of Works], Rostovskii Gos. Univ., Rostov-on-Don, 1967, p. 96 (in Russian).
- 2. A. C. Pratt, Chem. Soc. Rev., 1977, 6, 63.
- 3. I. Kuruts and L. L. Rodina, in Sovremennye problemy organicheskoi khimii [Modern Problems of Organic Chemistry, Collection of Works], Izd-vo Leningrad, Gos. Univ., Leningrad, 1987, 6, 72 (in Russian).
- 4. V. A. Smirnov and V. B. Nazarov, Pribory i Tekhn. Eksperim. [Equipment and Experimental Techniques], 1975, No. 13, 260 (in Russian).
- R. N. Nurmukhametov and N. A. Vasilenko, Zh. Fiz. Khim., 1975, 49, 3053 [Russ. J. Phys. Chem., 1975, 49 (Engl. Transl.)].
- 6. E. Fischer and Y. Frei, J. Chem. Phys., 1957, 27, 808.
- 7. N. J. Turro, Molecular Photochemistry, W. A. Benjamin, New York, 1965.

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