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Photochromism of single crystals of arylhydrazide derivatives

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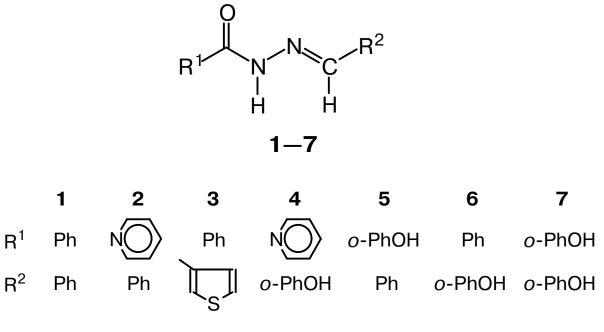
Photochromic transformations in single crystals of hydrazides due to *trans—cis*-isomerization were found. The presence of the hydroxyl group in the *ortho*-position of the benzylidene fragment completely precludes photoinduced isomerization in the crystalline state.

Key words: photochromic transformations, arylhydrazides, single crystals, *trans—cis*-isomerization.

Photochemical transformations in the solid state evoke interest from the viewpoint of fundamental studies and possible practical applications, in particular, for optical recording of information.[1,2] Due to close packing of photoactive molecules in crystal, new cells with high density of information recording can be created on the basis of photochromic crystals. Photochromic transformations in the crystal state have previously been observed in cyclization of diarylethenes,[3] keto-enol tautomerism,[4] and in photochromic spirooxazines.[5]

Diaryl derivatives of hydrazides with the general formula R^1—CO—NH—N=CHR^2 undergo *trans—cis*-isomerization about the C=N double bond under irradiation in solutions,[6] and the absorption spectrum of the photoinduced form lies in a longer-wave region than the spectrum of the initial molecules. Thus, diarylhydrazides show promise for recording the optical information.

In this work, photochromic transformations in single crystals of arylhydrazides **1—7** were studied.



Experimental

Single crystals of compounds **1—7** are small in size (surface area of the face <1 mm^2); therefore, a special device based on a Unicam SP-800 spectrophotometer was developed for studying their optical properties. The device was placed in the cell compartment and consists of the following parts: (a) a quartz cylindrical lens focusing a narrow vertical beam to form a spot with a small surface area, (b) a set of holders of a single crystal with holes 0.2—1.0 mm in diameter, and (c) a quartz lens focusing the light to a photoamplifier. This system makes it possible to study the absorption spectra of single crystals with a surface area of the face of 0.04—1 mm^2. Samples were irradiated with a DRSh-1000 lamp using a set of glass light filters directly in the cell compartment without changing crystal orientation.

Single crystal samples were irradiated with the light in the region of spectral absorption of the substance. Under these conditions, photochemical transformation occurs only in the near-wall layer of the crystal. However, despite the nonuniform distribution, this method allows one to solve the principal problem on studying photochromic transformations in single crystals.

Arylhydrazides **1—7** were synthesized from hydrazides of acids and corresponding aldehydes by heating for 0.5 h in anhydrous EtOH on a water bath.[6]

Results and Discussion

The wavelength for the *trans—cis*-transition of arylhydrazides **1—7** is 313 nm, and that for the *trans—cis*-transition of compounds **1—3** is 405 nm; no photochemical transition of single crystals **4—7** was observed. The experimental results are presented in Fig. 1 and Table 1. As follows from Fig. 1, photochromic transformations also occur in the crystalline state, and similarity of the absorption spectra of the induced form in an alcoholic solution and in crystal indicates that the *trans—cis*-isomerization of the hydrazide is observed in crystal. This is confirmed by the reverse transition to the ground state that occurs under irradiation at the absorption band of the induced form (405 nm) as in solution.[6] The reverse *cis—trans*-transition in crystal also occurs in the dark at room temperature (see Table 1).

Photochromic transformations are also observed for other hydrazide derivatives (see Table 1, compounds **1** and **3**). As in solution, the spectral properties of the

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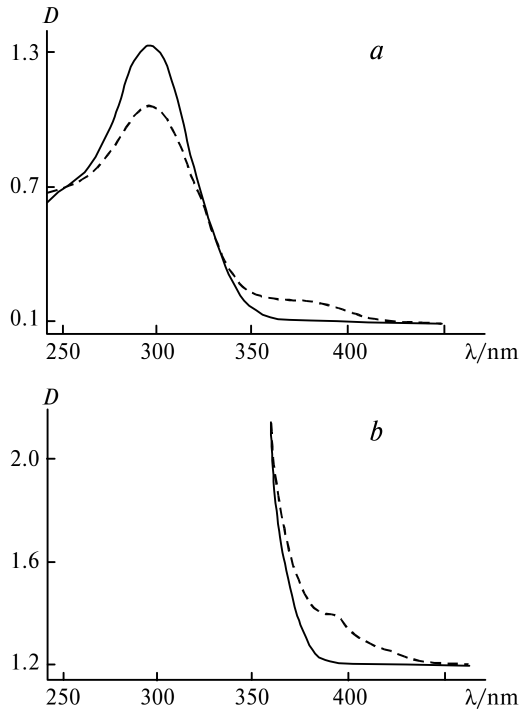

Fig. 1. Absorption spectra of isonicotinehydrazide (**2**) at room temperature before (solid line) and after irradiation with the light at λ = 313 nm (dotted line): *a*, in an alcohol solution; and *b*, in the crystalline state.

Table 1. Photoinduced transitions* in single crystals of hydrazide derivatives **1—3**

Compound	$t_{c\to t}$ /h	λ_{cis} /nm	$D_{cis}^{\max}$
1	Does not return, crystal grows turbid	390	0.2
2	4	400	0.2
3	1	420	0.47

* The time of *cis—trans*-transition under dark conditions ($t_{c\to t}$), absorption wavelength, and absorbance of the *cis*-form are presented (λ_{cis} and $D_{cis}^{\max}$, respectively).

photoinduced forms depend on the structure of the molecule. The presence of a heteroatom in the aromatic fragment increases the absorbance, which correlates with the optical properties of these compounds in an alcoholic solution.[6]

After fivefold reversible photochromic transitions, single crystals of compounds **2** and **3** do not change their properties, whereas the surface of the single crystal of compound **1** grows turbid upon repeated photochromic transformation due to decomposition of the single crystal surface, although the reversible photochromic properties are conserved.

The photochromic properties of the substituted *ortho*-hydrooxyazomethine single crystals have previously been studied[4,7] in which the hydrogen transfer due to keto-enol tautomerism was observed. We synthesized diarylhydrazide molecules with the hydroxyl substituent in the *ortho*-position of the benzylidene fragment in which the intramolecular hydrogen transfer is also possible (compounds **4**, **6**, and **7**). The presence of hydroxyl groups can impede the photoisomerization of molecules, which is observed in alcoholic solutions: the quantum yield of *trans—cis*-isomerization in compounds **5** and **6** is much lower than that in compound **1**.[6] The presence of the hydroxyl group in molecules **4**, **6**, and **7** completely prevents the photoinduced transition in the crystalline state. This can be explained by the strong intramolecular hydrogen bond between the H atom of the hydroxyl group and the N atom of the N=C group, which is confirmed by X-ray diffraction data for these crystals. Crystals **5** do not either exhibit photochromic transformations, although the OH group participates only in the formation of the intermolecular hydrogen bond. This is resulted from the specific feature of the crystalline structure of compound **5**.

Thus, single crystals of arylhydrazides are systems that allow optical information recording based on the effect of *trans—cis*-photoisomerization, and the photochemical properties of these compounds can be affected by inter- and intramolecular hydrogen bonds.

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