Inverse photochromic systems based on ketoenamine derivatives

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The results of studies into inverse photochromic systems (systems with negative photochromism) based on ketoenamines and ketoenehydrazines of benzo[\textit{b}]annelated heterocycles and their acylated derivatives carried out at the Institute of Physical and Organic Chemistry at the Rostov State University in the last two decades are summarized.

Key words: photochromism, ketoenamines, ketoenehydrazines, \textit{N}-acylated ketoenamines, \textit{Z}/\textit{E}- and \textit{E}/\textit{Z}-photoisomerization, acylotropic rearrangement.

Photochromism means a reversible, electromagnetic radiation-induced transformation of a bi-stable molecule between isomeric states \textit{A} and \textit{B} (Scheme 1), which are characterized by different spectral-luminescent and some other properties\textsuperscript{1—8}.

\begin{equation}
\text{Scheme 1}
\end{equation}

The back transformation of form \textit{B} into \textit{A} can take place in different ways: photochemically (on irradiation with light with a different wavelength and the energy \(E_2 = h\nu_2\)), on exposure to magnetic or electric field, on changing the temperature, or on treatment with chemical agents. In most cases, colorless or pale-yellow form \textit{A} is converted into colored form \textit{B} (positive photochromism). Negative photochromism (\(\lambda_{\text{max}(A)} > \lambda_{\text{max}(B)}\)) is observed much more rarely and these systems are called inverse photochromic.\textsuperscript{2,3}

The action of monomolecular inverse photochromic systems is based on simple chemical transformation mechanisms; most often, light-induced geometric \textit{E}/\textit{Z}-isomerization at the \textit{C}=\textit{C} bond (Scheme 2).\textsuperscript{9—13}

\begin{equation}
\text{Scheme 2}
\end{equation}

Studies of the transformations of inverse photochromic compounds shown in Scheme 2 are topical not only as regards the development of the fundamental views on the nature of photochromism,\textsuperscript{1—4} but also owing to their useful properties, because these systems can be used to accumulate light energy,\textsuperscript{1,6} as materials for information receiving and processing or molecular switching of optical signals,\textsuperscript{14—18} and for the design of new photochromic chemosensors for metal cations.\textsuperscript{19,20}

Geometric isomerization of heterocyclic ketoenamines

The photochemical \textit{Z}/\textit{E} and \textit{E}/\textit{Z}-isomerization at the \textit{C}=\textit{C} bond has been an object of intensive studies during the last decades.\textsuperscript{6,9,12,13,21—23} However, published data on the photoisomerization at the \textit{C}=\textit{C} bond conjugated with keto or amino groups are less abundant. Exceptions are indigo, thioindigo and its derivatives (see, for example, a review,\textsuperscript{6} chapter 2).

Although some attempts have been made to relate the presence of an intramolecular hydrogen bond (IMHB) to the possible existence of various molecules including ketoenamines, as \textit{E} or \textit{Z} isomers and to possible \textit{E}/\textit{Z}-isomerization in the ground or electronically excited state,\textsuperscript{24—27} the foundation for the study of ketoenamine isomerization was laid in Ref. 28, where the theoretical, spectroscopic, and X-ray diffraction data\textsuperscript{29—34} concerning the structures of ketoenamines derived from benzo[\textit{b}]annelated five-membered heterocycles were related to different contributions of the bipolar resonance structures \textit{A} and \textit{B} (Scheme 3). Whereas ketoenamines with \(X = O\) tend to exist as the \textit{Z} isomers in the crystal phase,
for compounds with \( X = S \) and NMe, \( E \)-structure is typical. The contribution of form B increases with a growth of the electron-releasing properties of the heteroatom in the series CO < CH2 < O < S < Se < NMe, which promotes the formation of a strong intramolecular hydrogen bond and a quasiaromatic ring. The conclusion that, among physicochemical methods (certainly, except for X-ray diffraction), IR spectroscopy provides the most clear data on the fine structure of molecules 1 is especially important.

The decrease in the stretching frequency of the ketoenamine fragment clearly corresponds to the degree of polarization of the conjugated bonds. These theoretical statements were soon verified in practice. Indeed, 2-(\( N \)-phenylaminomethylene)-1-methylindol-3(2H)-one (1f, \( X = NMe \)) exists only as the \( E \)-ketoenamine form with a strong IMHB and does not exhibit photochromic properties. Compounds 1a,c,d exist in solutions as an equilibrium of \( E \)- and \( Z \)-forms (Scheme 3, upper line) the position of which depends on the nature of the heterocycle annelated to the ketoenamine fragment. The rate constant for the thermal \( E/Z \)-isomerization decreases in the sequence of heteroatoms \( X = O > CO > S > NMe \), with an increase in the solvation capacity of the solvent, and in the presence of acid or base catalysts. For ketoenamines 1, the photochemical \( Z/E \)-isomerization is observed for \( X = O \), \( E/Z \)-isomerization takes place at \( X = S \), and reversible \( E \Leftrightarrow Z \)-isomerization is typical of \( X = CO \).

Scheme 3

In the latter cases, irradiation induces a minor hypsochromic shift (3—4 nm), which allows one to consider systems 1a,d to be the first examples of inverse photochromic ketoenamines.

In order to increase the difference between the absorption peaks of \( E \)- and \( Z \)-forms, we studied ketoenamines containing bulky groups at the exocyclic carbon atom.

2-Benzoyl-3-hydroxybenzo[\( b \)]thiophene imines 2 exist in the ketoenamine form \( E-3 \), irrespective of the type of substituent \( R \) or solvent polarity (Scheme 5).

Scheme 5

Attention is attracted by the fact that the stretching frequencies of the carbonyl group of ketoenamines 2 are much lower (\( \Delta \nu = 35—85 \text{ cm}^{-1} \)) than the \( \nu_{C=O} \) of imines 1d (\( X = S \)). On the one hand, this attests to a more probable \( E \)-structure of compounds 2 with a strong IMHB, and on the other hand, this is indicative of a substantial contribution of bipolar structures of types A and B (see Scheme 3) to the molecular geometry. Indeed, only in the case of \( p \)-nitrophenylimine 2, which has the smallest \( \Delta \nu_{C=O} \) compared to \( p \)-nitrophenylimine 1 (\( X = S \)), can one observe slight, thermally reversible spectral changes (the hypsochromic shift of the absorption peak \( \Delta \lambda_{max} \approx 1—2 \text{ nm} \) and hypsochromic effect \( \Delta \epsilon_{max} \approx 3—5\% \)) corresponding to \( E/Z \)-photoisomerization (heptane solution). Thus, the introduction of a phenyl group to the exocyclic carbon atom does not promote \( E/Z \)-isomerization; moreover, this appreciably stabilizes the \( E-2 \) form due to the contribution of bipolar resonance structures. Therefore, in further search for inverse photochromic systems capable of photoinduced \( E/Z \)-processes, only alkyl substituents were introduced in ketoenamine molecules.

According to UV, IR, and \( ^1\text{H} \) NMR spectroscopy, 2-acetyl-3-hydroxybenzo[\( b \)]thiophene imines 3, exist in the ketoenamine form \( E-3 \), irrespective of the type of substituent \( R \) or solvent polarity (Scheme 5).