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Bicyclic Derivatives of Aziridine - Materials for New Indicators of Radiation

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Abstract - The article is devoted to the study of some bi-and tricyclic derivatives of aziridine as materials for newindicators of ionizing radiation. To create high sensitive materials some aspects of photo induced ring opening processes in aziridine derivatives in ethanol solutions and in polymeric matrix were studied and two steps character of the processes investigated was established. Two types of radioindicators were suggested and preliminary tested. The new way of synthesis of radiochromic derivatives of aziridine was developed and series of target compounds synthesized.

Key words : aziridine derivatives, photochromic compound, radiochromic compound, indicator of radiation, radiation

Introduction

The usually used organic scintillators and detectors are based on the conversion of radiation into light and subsequent recording with photodetector. Most of the instruments operating on this principle register total dose (or intensity) of the radiation, regardless of its source and direction [1].

Another method of detection is concerned with the use of organic substances that can change their color under the action of ionizing radiation. These can be compounds which respond directly to the radiation (radiochromes) or to UV and visible light (photochromes).

Photo-or radiochromy, i.e. a conversion of one organic compound into another under electromagnetic or ionizing radiation correspondingly, is one of most interesting effect in chemistry which is used in practice for creation of light control systems, information recording or sun energy accumulation [2]. A difference between absorption wave-lengths of starting compounds and photo (radio) induced form determines the color change of photochrome. In many cases a reverse conversion which can proceed as a dark process or under irradiation (heating) is possible.

During the last years a series of such organic compounds has been discovered and studied [3-6], but we concentrated our attention on bi-and tricyclic derivatives of aziridine 1,2,3 :

Bi-and tricyclic derivatives of aziridine have attracted attention of researchers since the seventies of the last century. But today there is no whole conception of mechanism of the photochromic processes in such compounds.

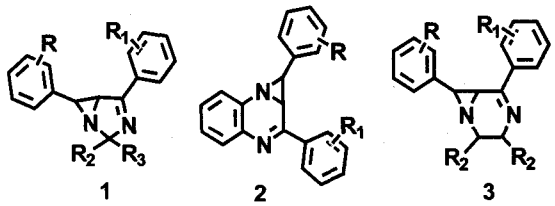


Fig. 1. Some bi-and tricyclic aziridine derivatives.

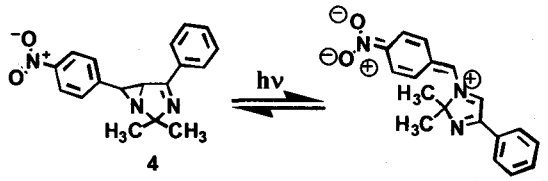


Fig. 2. Ring opening process in the derivatives of bicyclic aziridine.

The dependence between structure and properties, behavior of aziridine in polymeric matrix and in solution are studied very poorly.

According to the literary data [7-10] photochromy of bicyclic aziridines is connected with ring open process and formation of bipolar colored form (Fig. 2). At this, aryl substituted aziridines are unique compounds due to the presence of possibility of charge delocalization at phenyl rings. Such delocalization stabilizes the open form and assists in color intensification. From the other hand these compounds can be synthesized from easily available organic compounds [7, 11].

Before our investigations photochromy of bicyclic derivatives of aziridine was studied in crystalline state only. At this, an irradiation of the crystals of 1-3 leads to appearancein UV spectra of long-wave absorption band at ca. 600 nm which disappears after stopping the irradiation. This corresponds to a deep-blue color of the photoinduced form.

Results and Discussion

We concentrated our investigation on the study of photochromy of nitro-substituted derivatives of the aziridine 4, which according to literary data [7-10] possesses the highest sensitivity to UV irradiation. The most interesting problem was to study its behavior in ethanol, hexane solutions and in polymeric matrix.

It was found that under UV irradiation at 313 nm of ethanol solutions of this aziridine fast photochromic processes proceed (Fig. 3). The slow reverse process also was fixed in solutions-double multiplex collapse of absorption

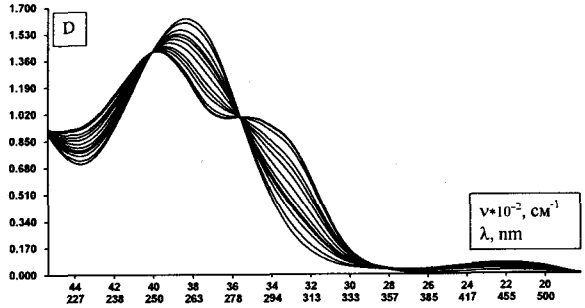


Fig. 3. Change of UV absorption spectrum of aziridine 4 in ethanol under UV irradiation (313 nm).

band of photoinduced form was observed during 2 h.

There is an explicit inconsistency between long-wave absorption bands in solid (ca. 600 nm) and in ethanol (ca. 420 nm). Thus, we have two different photo induced products.

Additional information about photochromic processes was obtained when we studied the behavior of the aziridine 4 in polymer matrix. UV irradiation of such composite is accompanied by appearance of absorption band at 600 nm and deep-blue coloration of the sample. After that this band collapses and spectral image becomes close to solution one- we observed an increase of absorption band at 420 nm (Fig. 4) :

The results obtained allow to assume the two steps mechanism of photochromic process in bicylic aziridine under UV irradiation. At this, bipolar structure corresponds not to the deep-colored form observed in crystalline state, but to the yellow compounds found in solvents. The structure of the deep-blue form maybe

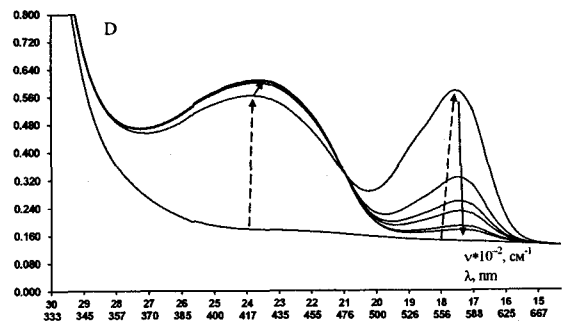


Fig. 4. Change of UV absorption spectrum of aziridine 4 in polystyrene matrix under UV irradiation (313 nm).

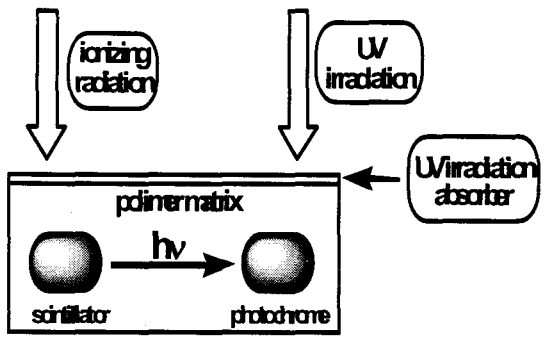


Fig. 5. Principal scheme of the first type indicator.

ion-radical or biradical, but this assumption calls for more detailed investigations.

In the context of the present work we considered two ways to visual indicators of ionizing radiation based on bicyclic aziridine derivatives.

The first is using aziridine as a photochromic compounds (first type indicator). This type of indicator contains photochrome and scintillating additives. At this the minimal overlapping of absorption bands of a scintillator and a photochromic compound, and maximal overlapping of the emission band of a scintillator and absorption band of a photochrome are required. Irradiation of polymeric composite leads to the scintillator's emission which can be absorbed by photochrome with changing of its color. To avoid the influence of UV irradiaton directly on the photochrome the indicator has to be covered by a special UV absorber (Fig. 5).

A serious preclusion for the high sensitivity of such indicators is concerned with the solid-phase character of aziridines photochemistry. In this connection it was possible to use only suspensions of photoactive compounds, but not real, highly transparent solutions.

Another way to create radio sensitive indicators is concerned with an idea of combining both photochromic (aziridine) and radiophoric (polyarene) fragments in one molecule (second type indicator). In this case we can use aziridine in solid (crystalline) state (Fig. 6).

The choice of objects for synthesis was determined by the aims of investigation (at least one of the substituents should have polyarene nature), and also by the previously obtained data stating that nitro-derivatives have the highest photosensitivity and depth of photo-induced form coloration. We have developed a new approach involving Suzuki reaction concluding interaction of halogen derivatives of bicyclic aziridines 5-6 with arylboronic acids 7-8 in the presence of palladium catalyst (Fig. 7). We synthesized a series of derivatives of aziridine 9-11. It should be mentioned that it was actually the first case of use of this reaction in aziridine chemistry.

Preliminary testing of radiochromic properties of the compounds otained showed that derivatives 9-11 havesufficiently high sensitivity towards ionizing radiation (under the action of β-and X-rays) and can be used for creation of radio sensitive indicators of the second type.

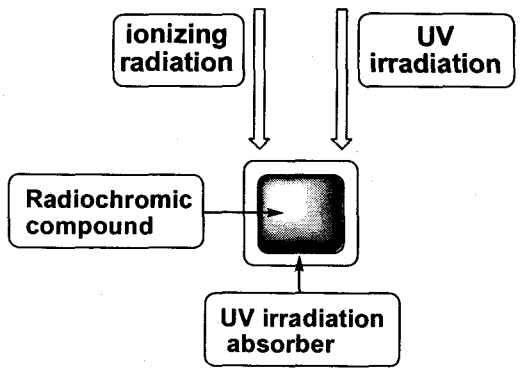


Fig. 6. Principal scheme of the second type indicator.

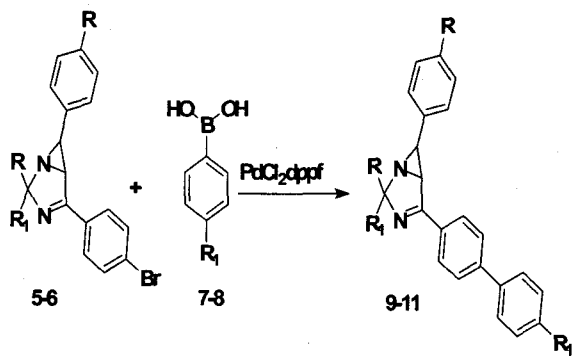
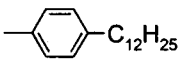
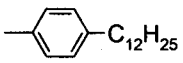


Fig. 7. General scheme for obtaining of radiochromic derivatives of aziridine 9-11.

Table 1. List of substituents of compounds 5-11.

Compound	R	R_1
5	H	-
6	NO_2	-
7	-	H
8	-	
9	H	H
10	NO_2	H
11	NO_2	

Conclusions

1. Bi-and tricyclic derivatives of aziridine are the potential materials for creation of ionizing radiation indicators.
2. Photo induced ring opening processes in aziridine derivatives in ethanol solutions and in polymeric matrix have two steps mechanism.
3. Two main type of indicators based on bicyclic aziridines can be suggested :
   - plastic composite containing photochromic aziridine and scintillating additive
   - radiochromic aziridine encapsulated in UV absorbing shell
4. New radiochromic derivative of aziridine for the second type of indicator were synthesized by Suzuki reaction.

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