PHOTOCHEMICAL FORMATION OF AZODYES IN SOLUTIONS AND FILMS CONTAINING AZENES AND AZOCOMPONENT

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The experimental researches of photochemical azodye derivation in solutions and films containing azene (pentazene or triazene) and azocompound have shown that the photochemical processes take place in associates of the different structure derivated by indicated components. The association of components is stipulated by interaction between completely filled azenes n-MO and unfilled n-MO of azocompounds molecule formed after the $sp^2 \rightarrow sp^3$-rehybridization of its active point and consequent reexcitation of a molecule. The photochemical process represents intraassociates photoregrouping of links with derivation of azodye molecules and methylamine.

Keywords: azocomponents, pentazene, triazene, azodyes, associate, rehybridization, photoregrouping.

It is known, that azodyes are being derived at interaction between diazonium salts and azocomponents of phenol (or methene) type in the alkaline or neutral environment:
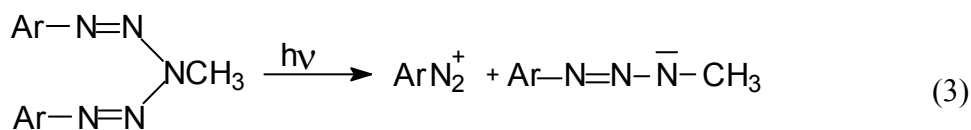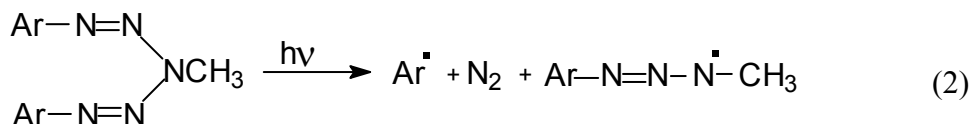
$$R{-}Ar{-}\overset{+}{N_2} + R_1{-}ArOH \xrightarrow{\;NH_3\;} R{-}Ar{-}N{=}N{-}Ar\underset{OH}{\overset{R_1}{\diagup}} \qquad (1)$$
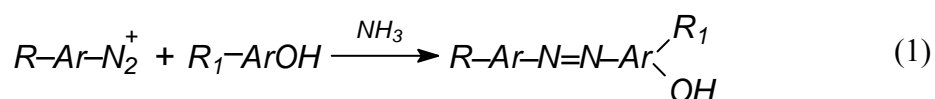
where R and R_1 - assistants in appropriate aryl ($\grave{A}r$) fragments [1,2]. This response is used at manifestation of the image after exposure of diazotype materials. For the first time possibility of photochemical obtaining of azodyes in light-sensitive layers azocomponent and azene containing, as a rule, 1,3-diaryltriazene or 1,5-diaryl-3-alkylpentazene was depicted in [3,4]. The discovery of this response has allowed to offer new sort diazotype of copy materials - negative diazotype materials. The learning, of photoprocesses in liquid and hard water-alcohol solutions above evocative derivative of the azenes class held by us earlier [5,6] has served as a starting point in a research of mechanisms of azodyes derivation in azene-azocomponent systems, which description in literature is absent.

Azenes (1,5-di-(p-methoxyphenyl)-3-methylpentazene (P_1); 1,5-biphenyl-3-methylpentazene (P_2); 1,3-bi-(p-methoxyphenyl)-triazene (Tr_1), 1,3-biphenyl-triazene (Tr_2)) used in operation are synthesized on known techniques [7,8]. The connections of phenol and methenes types, released by firms of a chemical industry for obtaining azodyes, were selected as azocomponents, namely: hydrazide and β-oxyethylamid 2-oxy-3- naphthoic of acid (AC_1 and AC_2, accordingly), resorcin (AC_3), 3-methyl-1-phenylpirazolone (AC_4).

Photolysis of solutions and films was carried out by a UV-light of a mercury lamp ДРШ-250-2 with use of light filters. The spectral changes in investigated objects were registered with spectrophotometer "Specord-M-40". The identification of azodyes, formed at an irradiation of containing azene and azocomponent solutions and films, was carried out by matching their absorption spectrums and absorption spectrums specially of synthesized dyes.

Described in [3,4] azodyes derivation at of pentazene (P_1, P_2) or triazene (Tr_1, Tr_2) photolysis in presence of azocomponents may be explained presumptively due to possibility of a simultaneous course of an electronic photodissociation N-N of bond in azenes on two mechanisms - homolytic and heterolytic:

$$Ar-N{=}N\diagdown\atop Ar-N{=}N\diagup NCH_3 \xrightarrow{h\nu} Ar^{\cdot} + N_2 + Ar-N{=}N-\overset{\cdot}{N}-CH_3 \qquad (2)$$

$$Ar-N{=}N\diagdown\atop Ar-N{=}N\diagup NCH_3 \xrightarrow{h\nu} ArN_2^{+} + Ar-N{=}N-\overset{-}{N}-CH_3 \qquad (3)$$

If diazonium cation was derived on response (3), it would enlist response of a combination with present in azocomponents solution, derivating azodye. The data obtained by us at research of photochemical transformations of azenes molecules in solutions and films [5,6], uniquely confirms the to absence of such response and, therefore, only about homolytic splitting of N-N-bonds in azenes molecules. The addition of azodyes ethanolic solutions to azenes ethanolic solutions does not result in change of the form and intensity of their long-wave absorption band, i.e. there are no reasons for the change of the mechanism of a photochemical dissociation of azenes. However, it is revealed experimentally, that the irradiation of solutions of azenes in mixture with azocomponents by a light with a wavelength appropriate to the long-wave absorption band of azenes, results in derivation azodyes which are spectral identical to a dye obtained at response of azo coupling of appropriate diazonium salt and azocomponent (fig.1). On fig.1 the absorption spectrums of p-methoxyphenyldiazonium tetrafluoroborate salt (p-MPD), azocomponent AC_2 and azodye (AD), obtained by a azocoupling of p-MPD, AC_2, pentazene P_2 and azodye, obtained at photolysis of P_2 solution with AC_2 are given. The detailed study of the process of photochemical derivation azodye made it possible to state a number of the facts:
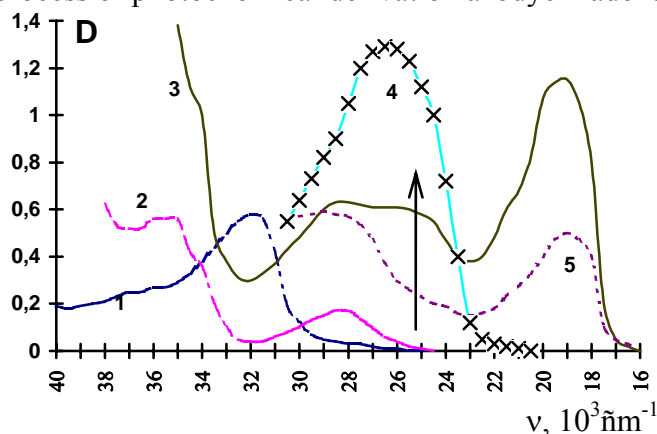

Fig.1. Absorption spectrums of ethanolic solutions: 1- p-MPD (10^{-4} molls /l), 2 - AC_2 (5 (10^{-5} molls /l), 3 - AD (5 10^{-5} molls /l), 4 - P (3 10^{-5} molls /l), 5- after an irradiation of solution containing P (3 10^{-5} molls/l) and AC_2 (2,1 (10^{-5} molls/l). The arrow indicates a wavelength of an irradiating light.

First et all, azodye is being derived at azenes photolysis at the presence of all azocomponents of a phenolic type, but only some - of a methene type;

Secondly, azodye is being derived at an irradiation even limiting . of diluted solutions (concentration of both components does not exceed 10^{-6} molls / l);

Thirdly, the output of azodye reaches 200 % from the pentazenes initial concentration and 100%- triazenes;

Fourthly, the output of azodye is being saved at change PÍ of the environment.

This data allows to suppose, that the derivation of azodyes takes place in associate, formed owing to dark interaction between azenes molecules and azocomponents. As a position and intensity of the absorption band appropriate $\pi{\rightarrow}\pi^*$- transitions in a molecule of azene, do not depend on presence of azodyes in solution, the derivation associate takes place, apparently, at interaction completely filled n-orbital of azene with free molecular orbital of azocomponents.

The research of dependence of optical density of the derived azodye (AD) from a relation of concentrations of azocomponent and pentazene at constant concentration of the latter (fig.2) demonstrates, that the derivation of associates, including a molecule pentazene and one or two azocomponents molecules should be considered as the most probable. As it is visible from a

fig.2, at small concentrations of azocomponents (10^{-6}-10^{-4} molls/l) the output of azodyes makes 2 molecules of a dye on one pentazene molecule.

Further increase of azodyes concentration ($2 \cdot 10^{-4}$- $5 \cdot 10^{-3}$ molls/l) results in lowering an output of a dye up to a one and a half of molecules on one molecule of pentazene.
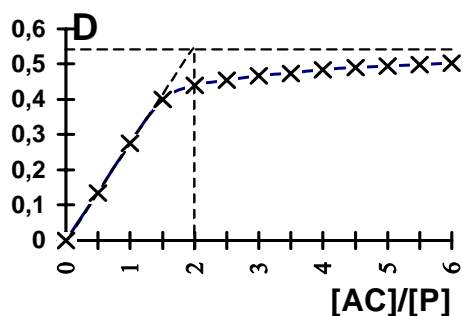

Fig.2. Dependence of optical density AD from a relation [AC] / [P] at [P] = 3,2 10^{-5} molls /l.

The calculations were fulfilled taking into account a fraction of light absorbed by azocomponent itself during the increase of its concentration in solution. Decrease of a photoyield of dye testifies that the existence of associate P:AC = 1:3 is possible, but the presence of the third molecule of azocomponent leads to the appearance on the second path of an electronic photodissociation which not result in azodye derivation. It is possible to introduce aforesaid as the scheme:

$$P + AC \xrightleftharpoons{k_1} F_1$$

$$F_1 + AC \xrightleftharpoons{k_2} F_2 \qquad\qquad (4)$$

$$F_2 + AC \xrightleftharpoons{k_3} F_3$$

where F_1, F_2, F_3 - associates P:AC = 1:1, P:AC = 1:2, P:AC = 1:3 accordingly,

$$F1 \xrightarrow{h\nu} AK$$

$$F2 \xrightarrow{h\nu} 2AK \qquad\qquad (5)$$

$$F3 \xrightarrow{h\nu} 1,5AK$$

At photolysis of associate F1 with a quantum yield φ_1 one molecule of azodye and one molecule triazene is being derived, the photolysis F_2 and F_3 results in derivation, accordingly, two and 1,5 molecules of azodye with quantum yields φ_2 and φ_3. derivation The photoresponse which appears at F_3 photolysis and is competing to azodye can be realized as follows:

$$F_3 \xrightarrow{h\nu} AK+Tr \qquad\qquad (6)$$

It was fixed experimentally, that the photolysis of pentazene at the presence of surplus of azocomponent (AC:P > 10) results in quantitative derivation of anisole, according to the second variant of response (6).

The k_1, k_2, k_3 values were estimated from an experimental data obtained during the research of rate of photolysis of the diluted solutions of pentazene ($3,2 \cdot 10^{-5}$ molls / l) and rate of derivation of azodye in these conditions at constant concentration of pentazene and different concentrations of azocomponent. It was shown, that at small azocomponent concentrations (P:AC = 10:1) constant of rate of photolysis of pentazene (k_o) is constant. At the same time constant of rate of azodye derivation with increase of concentration of azocomponent is sharply magnified, run up to a maximum at [AC] = $4 \cdot 10^{-6}$ molls /l, that testifies to appearance in solution associate F_2 instead of F_1 without change of a rule: the main body of pentazene remains nonassociated. The preferential existence of associate as F_2 is possible, if the value of a constant of association k_1 is significantly less then k_2, $k_2 \cdot [AC]_o > 1 + 2k_1[P]$, where $[ÀC]_o$ - entered concentration of azocomponent. By substitution of concentrations is discovered: $k_2 > 2,5 \cdot 10^5 + 15 \cdot k_1$. From dependence of the value of optical density of azodye, formed at

photolysis, from concentration of azocomponent, at its small values it follows, that all molecules of azocomponent are associated with pentazene. It is possible, if $k_1 > 10^5$ l/molls. Then $k_2 > 2 \cdot 10^6$ l/molls. The associate F_3 exhibits itself at concentrations of azocomponent, exceeding $2 \cdot 10^{-4}$ molls / l, therefore $k_3 > 5 \cdot 10^3$ l/molls. Using shown above k_1, k_2 and k_3 values the allocation of associates of different structure in solution with constant concentration of pentazene and variable azocomponent (fig.4) was calculated.


[AC], 10^{-6} molls / l
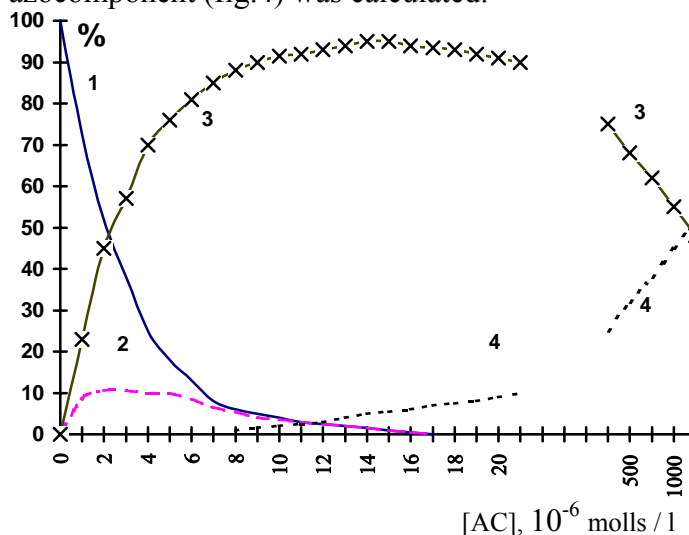
Fig.4. Dependence of relative concentrations of pentazene P_1 $(3,2 \cdot 10^{-5}$ molls/l)- 1 and it associates F_1 (2), F_2 (3) and F_3 (4) from concentration of azocomponent AC_2 in solution.

Using the speeds relation of azodye derivation at different concentrations of azocomponent it is possible to estimate values of quantum yields of photolysis associate $\varphi_1 = 0,26$; $\varphi_2 = 0,73$; $\varphi_3 = 0,42$. The lowering of a quantum yield of photochemical derivation AD with involvement of associate F_3 testifies in addition for the benefit of the scheme of responses (6).

To simulate the geometrical configurations of associates, fitting to experimental results the data of azenes molecules quantum-chemical accounts were used. So for pentazenes the possibility of existence of three isomeric forms having close values of energies was shown:

(7)
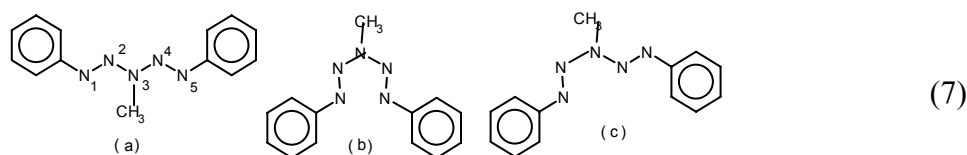
The isomer "b" has the lowest total energy. At room temperature 98,7 % of molecules of pentazene have the configuration "b", configurations "a" and "c" have 0,7% and 0,6%, accordingly. Thus the atoms of nitrogen bear charges on themselves: on $N_{(1)}$ and $N_{(5)}$ -0,17e, on $N_{(2)}$ and $N_{(4)}$ -0,05e, on $N_{(3)}$ +0,36e. Irrespective of isomer all atoms in a molecule of pentazene are located in one plane.

The association of pentazene with azocomponent should first of all take place with involvement n-MO, localized on atoms $N_{(1)}$ and $N_{(5)}$ isomers "a" and "c". It is necessary to mark, that the operation of a light on such associate (as structure P:AC = 1:1, and 1:2) will not reduce to derivation of azodye, since the breaking of homolytic bond N-N in pentazene is followed by derivation of two pieces, first of which will be converted into ArH, N_2 and AC, and second - into triazene (it is possible, with saving of associate with of azocomponent in a case P:AC = 1:2).

The association on n-MO, localized on atoms of nitrogen $N_{(2)}$ and $N_{(4)}$ is possible for all isomers of pentazene, but it is most typical for isomer "b", since in this isomer the access to n-MO on atoms $N_{(1)}$ and $N_{(5)}$ is steric hampered. The constant of derivation of associates on $N_{(2)}$ and $N_{(4)}$ for isomers "a" and "b" should be considerably less, than similar on $N_{(1)}$ and $N_{(5)}$.

The irradiation such of associates by a light can lead to production of a dye, because the structure of its molecule is present latent already in associate. However, allowing the variance in values of associates production constants on external $N_{(1)}$ and $N_{(5)}$ and internal $N_{(2)}$ and $N_{(4)}$ atoms of nitrogen, it is possible at its best to suspect only possibility of such process alongside with the depicted above processes of production of pieces.

The steadiest isomer of pentazene "b" will form associate of structure P:AC = 1:1 and P:AC = 1:2 on n-MO of atoms of nitrogen $N_{(2)}$ and $N_{(4)}$. The accessibility of these orbital for the approach of the partner on associate ensures the large value of constants of association: k_1 and k_2. It is possible to explain a $k_1 < k_2$ relation, receivable from experiment, by polarization of pentazenes piece at derivation F_1, which one causes additional interaction at binding in associate of the second molecule of azocomponent. For the approach of the third molecule of azocomponent to localized on $N_{(1)}$ and $N_{(5)}$ MO there exist the significant sterical obstacles, owing to which the rate constant k_3 of of associate F_3 derivation is less significant k_1 and k_2. The affixture of the fourth molecule of azocomponent in conditions of experiment is not being watched.

The explanation of responses (6) with involvement of associate F_3 (isomeric form "b") is possible if to suspect, that the excitation of associate F_3 can relax or by a regrouping of bonds, characteristic for of associate F_2, or by isomerization in the form "c", which remains associated on to three ï-MO. Last associate fails quickly, losing àçîñîñòàâëÿþùåe, associated on atom of nitrogen $N_{(2)}$ and/or $N_{(4)}$. As the result the associate will be derived, in which one the course only photoresponses with derivation of one molecule AD and triazene à or at all without derivation AD is possible. If in such associate the bond on external atom $N_{(1)}$ or $N_{(5)}$ will disappear, the spontaneous isomerization of pentazene in the form "b" will come true. To confirm this we shall mark, that in absorption spectrums of photolysed solution which contained associates F_3, the accumulation ArH is being registered.

The quantitative values of constants of association allow to consider bond in associate rather strong, that is possible only in case of change hybridization atomic orbital of an active point of azocomponent (ortho-position) from sp^2 up to sp^3 with derivation unfilled orbitals and its interaction with completely filled n-MO of pentazene. The light absorption by a pentazene component of associates P:AC = 1:1 and 1:2 will reduce in a breaking of one ($N_{(2)}$ -$N_{(3)}$ or $N_{(4)}$ - $N_{(3)}$) or two of bonds simultaneously and azodye production by a regrouping of bonds in associate (Pèñ.3).

The mechanism of association.

It is known, that azocomponents take part in azo coupling response, which is a classic example of electrophilic substitution, where diazonium cation appears in a role of electrophil [9]. This response flows in alkalescent environment, in which one phenol exists in the form PhO^- instead of PhOH. The response goes on beam-lead carbon in a para-position of phenol. The response can be introduced as follows:

$$(8)$$
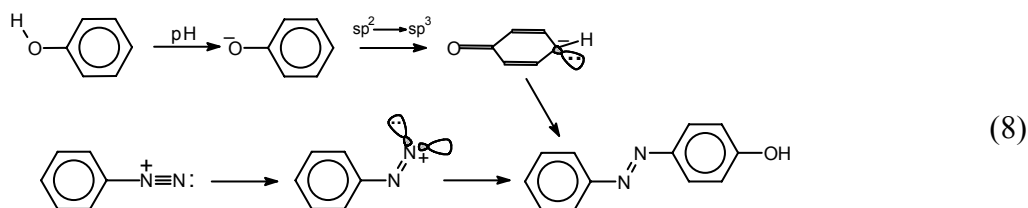
The derived AD stabilization is carried out due to moving of atom of hydrogen and rehybridization orbital in a phenolic piece.

There are no doubts, that the azocomponent association with pentazene is not described by mechanisms of electrophilic substitution, as a) azocomponent (phenol) associates with pentazene, being in an electroneutral state, b) the molecule of pentazene does not carry an electrical charge and c) the molecule of pentazene can put only completely occupied molecular orbital.

To understand the mechanism of intermolecular interaction in the azocomponent - pentazene system, we have paid attention to the mechanism of derivation of a chemical bond between atom

of oxygen and anions of halogens (for example, $Cl^- - O$) or inert gas atoms (for example Xe–O) [10].

We have tried to distribute the depicted mechanism of a chemical bond forming to a case, when not atoms but molecule are being interacted. The main requirement claimed to molecules is the presence in one molecule of a disjointed couple of electrons, one of which is localized on n-MO, and in other molecule - completely occupied n-MO. As to the first molecule, two cases are possible: a) electrons are separated in main triplet state of a molecule and b) electron separating it is possible to reach by nonsignificant modification of a molecule structure - by rehybridization of atomic orbitals of an active point of a molecule.

The molecular structures with two separated electrons in a ground state are known for us. This group of molecules includes in particular aryl and nitrene [11]:

$$\text{(9)}$$

By the way of reexcitation we shall convert these molecules into excited singlet state so that separated electrons (with the configuration $(\pi)^1(sp^2)^1$ in a case of aryl cation and $(\pi)^1(p_y)^1$ in a case of nitrene) have appeared to be coupled on π-MO and n-MO was completely released. Then let these activated molecules interact with a molecule of nitrogen *). In result there will be derived connections stable at room temperature in dark conditions: diazonium cation and azide:

$$\text{(10)}$$
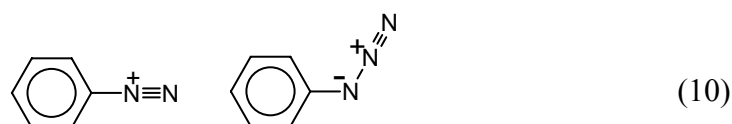
However, the dissociation energy of σ-bond in these molecules will be small: it equals approximately to 1 eV [15]. The excitation of a molecules which convert one electron with π-MO on σ*-MO (excitation in πσ*-state), will be followed by its effective dissociation [12, 13]. This effect is used for creation non-silver photographic (diazo type, vesicular, photodeformation etc.) materials [14].

The quantum yield of such dissociation always will be less then unit, because in πσ*-state the localization on distance is possible, it is more then equilibrium (fig.4), from where the relaxation is carried out into a metastable state (whence it is carried out in the field of a barrier) with the consequent change of distance to decreasing down up to equilibrium or increasing up to a complete dissociation. If the molecule is housed in rigid crystalline environment, the excitations relaxation will be carried out at smaller lengths of dissociating bond, that will bring to in lowering of quantum yield of an electronic photodissociation.

Let's esteem from these positions the association between azocomponent and pentazene. For manifestation of association it is necessary reexcitate (ΔE_1) a molecule of azocomponent (for example, AC_1 or AC_2) so that its active point get undergone $sp^2 \rightarrow sp^3$- rehybridization atomic orbital:

$$\text{(11)}$$
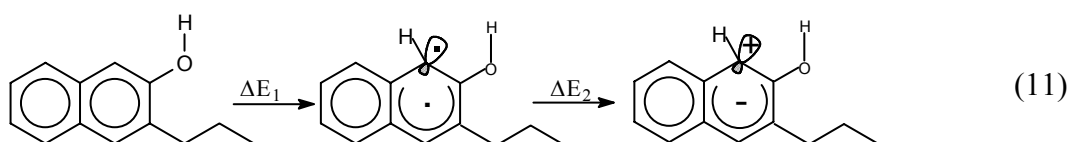
In this case one electron from π- system passes on to derived sp^3-MO, i.e. separating of electrons takes place. To get a donor-acceptor bond with pentazene it is necessary to reexcitate (ΔE_2, reaction (11)) localized sp^3- of an electron on π-MO of azocomponent. Naturally, such response is possible only at presence of interaction between the electronic system of

*) In a given example the molecule of nitrogen has not n-MO. At the same time it is possible to introduce real $2\sigma_u$ - and $3\sigma_g$ - molecular orbital of a molecule of nitrogen which are not being n-MO, as interacting among themselves n-MO owing to their close layout and presence of a resonance between them. The

azocomponent and n-MO of azene, supplying a cumulative prize of energy. The interaction will let to production of gentle (as there are required two reexcitation for rehybridization and ganging of electrons) complex of pentazene with azocomponent (fig.3). The consideration of the geometry of such an associate makes it possible to detect the steric obstacles for optimal forming of associate structure which supplies the greatest possible bond energy. It is an additional reason for obtain associate to be gentle. Nothing precludes the affixture of the second molecule AC to second n-MO of pentazene (on fig.3 the
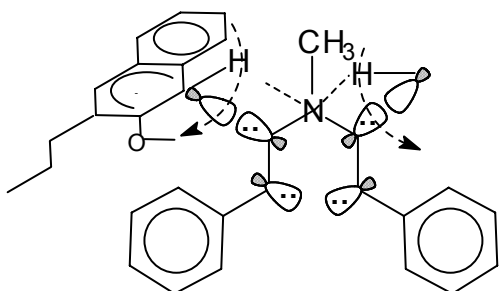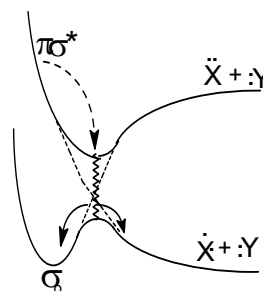

Fig.3. Structure of P-AC complex.

Fig.4. The diagram of energy states of molecules (complex).

small piece of the second molecule AC is rotined only). The relevant circumstance is that lower free molecular orbital (LUMO) of pentazene is localized on four atoms of nitrogen (except for central). The quantum jump of a electron on LUMO, which is breaking, will be followed with the rotation of a molecule pieces around of bonds $N_{(1)}$ -$N_{(2)}$ and $N_{(4)}$ -$N_{(5)}$, that will remove steric obstacles for the approchement between interacting orbital AC and pentazene. The interaction between atom of nitrogen $N_{(3)}$ and atom of hydrogen of azocomponent will be increased. The latter is followed by a regrouping of bonds, as a result of which one the atom of hydrogen is transferred on to atom of nitrogen, the bond $N_{(2)}$-$N_{(3)}$ and/or $N_{(4)}$-$N_{(3)}$ is broken, and azocomponent gains plane structure. The latter results in substantial growth of bond energy between
active points of pieces of associate and derivation of a stable molecule AD.

On fig.4 the mechanism of derivation of donor-acceptor bond between a piece X, carrying separated electrons, and piece Y which has n-MO is represented in a general view. From a figure it is visible, that at meeting of response components for derivation of a chemical bond it is necessary to overcome a potential barrier, which altitude is much lower than an excitation energy of oxygen atom. The altitude of a potential barrier for a breaking of a molecule is too small, as causes its evocative activity.

Thus, on the basis of the obtained experimental data on photochemical derivation of azodye in solutions and films containing azene and azocomponent it is possible to make following conclusions:

1) In solutions and films containing a molecules azenes and azocomponent, azene: azocomponent associate will be derived of different structure (1:1, 1:2, 1:3).

2) The derivation of associate is stipulated by interaction between completely filled n-orbital of azene and unfilled n-MO of a molecule of azocomponent, formed after $sp^2 \rightarrow sp^3$-rehybridization of its active point and consequent reexcitation of a molecule. The constants of derivation of possible associates are estimated.

3) The photochemical process may be represented as a intraassociative a photoregrouping of bonds with derivation of azodye molecules.

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ФОТОХИМИЧЕСКОЕ ОБРАЗОВАНИЕ АЗОКРАСИТЕЛЕЙ В РАСТВОРАХ И СЛОЯХ, СОДЕРЖАЩИХ АЗЕНЫ И АЗОСОСТАВЛЯЮЩИЕ

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Экспериментальные исследования фотохимического образования азокрасителей в растворах и пленках, содержащих азен (пентазен или триазен) и азосоставляющую, показали, что фотохимические процессы происходят в ассоциатах разного состава, образованных указанными компонентами. Ассоциация компонент обусловлена взаимодействием между полностью занятой n-МО азена и незаполненной n-МО азосоставляющей, образующейся после $sp^2 \rightarrow sp^3$- перегибридизации ее активной точки и последующего довозбуждения молекулы. Фотохимические процесс представляет собой внутриассоциатную фотоперегруппировку связей с образованием молекул азокрасителя и метиламина.

Ключевые слова: азокомпоненты, пентазены, триазены, азокрасители, ассоциаты, перегибридизация, фотоперегруппировка.

ФОТОХІМІЧНЕ УТВОРЕННЯ АЗОБАРВНИКІВ У РОЗЧИНАХ І ПЛІВКАХ, ЯКІ МІСТЯТЬ АЗЕНИ ТА АЗОСКЛАДОВІ

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Експериментальні дослідження фотохімічного утворення азобарвників в розчинах і плівках, які містять азен (пентазен, триазен) і азоскладову, показали, що фотохімічні процеси відбуваються в асоціатах різного складу, утворених вказаними компонентами. Асоціація компонентів зумовлена взаємодією між пованістю заповненою n-МО азена та незаповненою n-МО, яка утворюється після $sp^2 \rightarrow sp^3$-перегібридизації активної точки та наступного дозбудження молекули азоскладової. Фотохімічний процес є внутріасоціатним перегрупуванням зв'язків з утворенням молекул азобарвника та метиламіну.

Ключові слова: азокомпоненти, пентазени, триазени, азобарвники, асоціати, регібридизація, фотоперегрупування.