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PHOTODISSOCIATION MECHANIZM OF PENTAZENES MOLECULES

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This paper describes some results of experimental and theoretical investigations of photochemical processes in solutions of p-substituted diphenylpentazenes. The main photochemical process in liquid solutions is shown to be the photodissociation of a molecule due to relaxation of excitation into T ($\pi\sigma^*$)-state. This state is dissociative in methoxysubstituted diphenylpentazene case. But a potential barrier height is increased with decreasing of donor-acceptor properties of the substituent. Aryldiimine and triazenyl radicals are formed as a result of dissociation. The photodissociation is inhibited in full in solid (frozen) solutions and asymmetrical photoisomerization is the unique photochemical process.

The pentazenes solutions are specified by a intensive light-sensitivity. Due to this property they can found applications in various phototechnological processes [1-3]. Nevertheless, pentazenes have note received considerable attention in the literature, and photodissociation mechanisms of pentazene molecules do not determined until this time. That is why we report in this work some new results for investigated pentazenes, dealing with their structure, spectral and photochemical properties.

The basic investigated substances were p-substituted 1,5-diphenyl-3-methylpentazenes ($R-C_6 H_5-N=N-N(CH_3)-N=N-C_6H_5$, where R=H, OCH_3, NO_2). They were obtained by standard procedures [4] by reaction of azocoupling of corresponding diazonium salts with methylamine in cooled water solution.

Absorption spectra and photochemical properties of pentazenes solutions

The absorption spectra of pentazenes solutions were studied in works [5-7] previously. We obtained them with Specord UvVis and Specord M40 spectrophotometers.
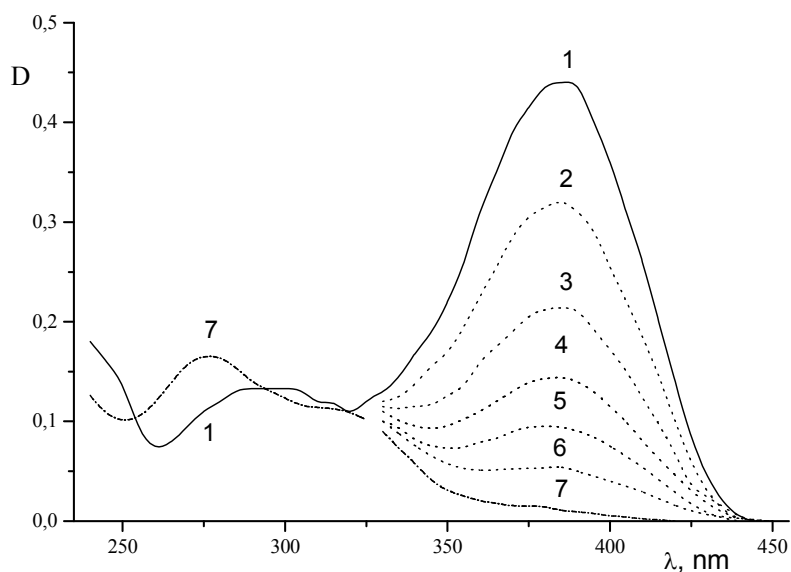

Fig.1. Absorption spectra of ethanolic solution of di-(p-methoxyphenyl)-3-methylpentazene [C=10^{-5} M/l] (1) before and after irradiation by UV-light (365 nm): 2 – 5 s, 3 – 10 s, 4 – 15 s, 5 – 20 s and 6 – 30 s; 7 - absorption spectrum of formatted triazene after irradiation of a starting pentazenes solution by integral light of a mercury lamp during 30 s.

In general the absorption spectra of pentazenes have an intense long wave-length band following with a much weaker short wave-length band. Peaks position depends on the nature of a substituentes in the phenyl cycle. Particularly, the maximum of the intense long wave-length band lies at 363 nm (27540 cm^{-1}) for unsubstituted diphenylpentazene as well as at 380 nm (26310 cm^{-1}) for p-OCH$_3$ and 362 nm (27625 cm^{-1}) for p-NO$_2$. S$_o$, the peak position of the absorption band correlates with electronnature of substituentes. An absorption band is shifted in a long-wave region of a spectrum (bathoromic). But we expected much more short wave-length shift in the case of nitro-substituted pentazene. However, the absorption band for the last almost shows no change , but it is broadening considerably.

Ethanolic solutions of pentazenes were irradiated by monochromatic light (λ=365 nm) mercury lamp. Photodecomposition of pentazenes was found results to the formation of corresponding triazenes, substituted benzenes and nitrogen:

$$Pz \xrightarrow{\ h\nu\ } Tr + N_2 + R - C_6H_5$$
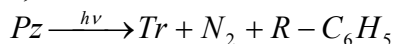
This conclusion was made on the basis of analyzes of absorption spectra of photolysis products.

Kinetics of pentazenes photodissociation were determined. They were compared with photolysis kinetic of a standard water solution of potassium ferrioxalate [K$_3$Fe(C$_2$O$_4$)$_3$] [C]=6$\cdot$10^{-3} M / l with the quantum yield φ =1,24. This allowed to find photolysis rates of these reactions and a quantum yield of pentazenes photolysis: φ=0,85 at R=H, 0,95 at R= OCH$_3$ and 0,02 at R= NO$_2$.

Quantum-chemical calculations

Quantum-chemical calculations pentazenes molecules were carried out using of a semiempirical method AM1 (method of self-consistent field] for interpretation of their spectral and photochemical properties. The configuration interaction (CI) between 10 filled and 10 free MO were taken for calculations. Nitrogen atoms in pentazene fragment were numbered from first to fifth (N$_1$, N$_2$, N$_3$, N$_4$, N$_5$). The total electrons energy was calculated for different geometrical configurations:

tt   tc   cc
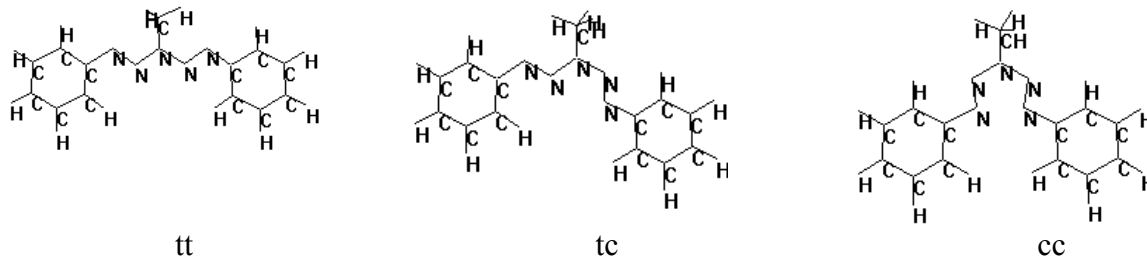
We marked the first configuration as tt (trans-trans) because of both parts of a molecule being in a trans-position concerning the central (N$_3$) nitrogen atom. And, accordingly, the second configuration will be tc (trans-cis), and the third - cc (cis-cis).

The calculations for pentazenes molecules have shown, that the contribution tt and ct-configurations into the total electron energy are considerably less then 1%. The transfer from tt and ct configurations into cc is realized without a potential barrier. So, practically all pentazenes are existing in cc-configuration.

Pentazenes molecular orbitals in cc-configuration

Molecular orbitals characteristics for all investigated pentazenes are shown in table 1.

-The MO structure, reduced in table 1, allows to forecast possible(probable) photochemical processes in pentazenes molecules. It is easy to see, that the quantum transition of an electron on the inferior free molecular orbital (LUMO) with high occupied MO (HOMO) should stipulate gyration of pieces of a molecule around N$_1$-N$_2$ and N$_4$-N$_5$ of communications(connections). It is the relevant background for existence of responses of pentazenes photoisomerization. Really, such processes were supervised in frozen (77 K) ethanolic pentazenes solutions [6].

Quantum transition on the σ*-MO have caused of molecules dissociation by break of weak bonds, namely N_2-N_3 or N_3-N_4 - bonds.

Table 1. MO characteristics of di-(p-methoxyphenyl)-3-methylpentazene, including operator of reflection action in a plane, perpendiculare to the molecule plane

# of MO	Tipe of MO	Activity of reflections operator	Localization of MO	Influence of MO on the N_2-N_3-bond	Influence of MO on the N_1-N_2-bond
Unoccupied molecular orbitals					
4	σ*	σ*	Pent. Group	Antibonding	Antibonding
3	π*	-π*	Phenyl	-	-
2	π*	π*	Phenyl	-	-
1	π_2*	π_2*	Delocalized	Antibonding	antibonding
0	π_1*(LUMO)	-π_1*	Delocalized	-	antibonding
Occupied molecular orbitals					
-1	π (HOMO)	π	Delocalized	Antibonding	bonding
-2	π	-π	Delocalized	-	Slow antibonding
-3	σ	-σ	Pent. Group	Bonding	bonding
-4	π	π	Phenyl	-	-

It is understandable, that the quantum transition between upper occupied MO and inferior by free MO will be accountable for long-wave absorption band. Reduced HOMO and LUMO concern to π-MO. By change of a substitute σ-MO can higher rise.

Because the processes of photoisomeric change of a molecules competing to processes of a photodissociation are possible(probable) we have conducted calculations of energy states of a pentazenes molecule depending on drift angle of planes of phenyl fragments concerning a plane of a molecule. At calculations guessed, that both pieces are wedged from a plane of a molecule simultaneously in miscellaneous or in one leg(party) (symmetric isomerization), or one piece (asymmetric isomerization) is turned only.

These calculations have shown, that the symmetric isomerization can not be implemented, as at simultaneous gyration of pieces of a molecule the energy of system increases for all exited states.
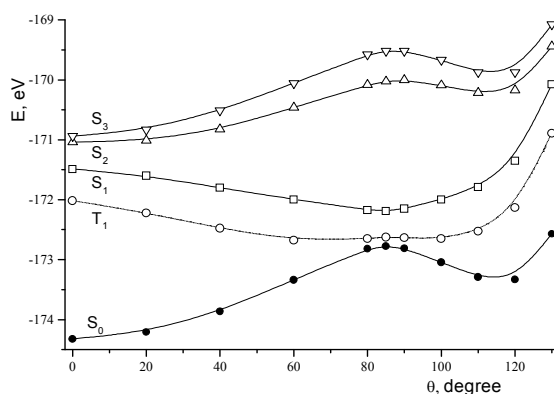

Fig.2. Di-(p-methoxyphenyl)-3-methylpentazene energy states dependence on an rotations angle relatively N_4 -N_5 -bond (asymmetrical isomerization).
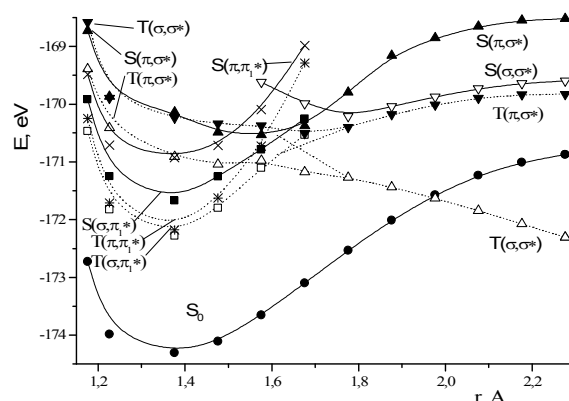
Fig.3. Energy diagram of the di-(p-methoxyphenyl)-3-methylpentazene molecule.

The gyration only of one piece of a molecule really calls depressing energy of electronic system in a T_1-state (fig. 2)., that is, the response of isomerization will flow past. It is

understandable, that such response will compete to response of dissociation of an activated molecule, which one will give in depressing quantum yield of its(her) dissociation.

Now we shall consider, how the energies of a molecule and separate therms will vary at magnification of distance between atoms N_2 and N_3. As the experiment demonstrates, that at photolysis of pentazenes will be made triazene, it testifies, that the molecules dissociate unbalancedly, that is, during dissociation the symmetry of a molecule is depressed. It also has stipulated carrying out of the indicated calculations.

We have conducted calculations for three *para*-substituted pentazenes , which one essentially differ by the photochemical properties: nitro-, methoxy- and unsubstituted pentazenes . The effects(results) of calculations for 1,5-di(p-methoxyphenyl) -3-methylpentazene are given in a fig. 3.

From fig.3 low singlet excited state (S_1) is $\sigma\pi_1^*$-state with force of an oscillator f1 = 0,004, state S_2 - $\sigma\pi_2^*$ with f2 = 0,035, state S_3 - $\pi\pi_1^*$ with f_3 = 0,560. At standard conditions in an absorption spectrum of pentazenes solutions we apparent intensive long-wave absorption band relevant to transferring in a S_3-state. In the paper [6] we have shown, that on a long-wave wing of absorption band there is a feeble strip, which one can be referred to initiation of a molecule in a S_1-state.

The analysis of a fig. 3 demonstrates, what at magnification of distance between atoms N_2 and N_3 of a states $T(\sigma\pi_1^*)$, $T(\pi\pi_1^*)$, $S(\sigma\pi_1^*)$ and $S(\pi\pi_1^*)$ are characterized by potential curves with penetrating holes. At the same time states $T(\pi\sigma^*)$, $T(\sigma\sigma^*)$, $S(\pi\sigma^*)$ and $S(\sigma\sigma^*)$ such of holes have no or have superficial holes. It is very important, as for tearing up N_2-N_3-bonds it is necessary, that the electron in an exited state of a molecule was localized on σ^*-MO (in our cases in $T(\pi\sigma^*)$-state), localized on sectional communication(connection). And the depressing of energy of the relevant therm at elongation of communication(connection) also provides indispensable localization of an electron. Therefore, for dissociation of a molecule the electron with LUMO in an exited state of a molecule should skip on σ^*_{N-N} -MO, that is, the process of relaxation or predissociation should be held.

Interaction between $T(\pi\sigma^*)$ and $T(\sigma\sigma^*)$- states is results that on distances 0,15-0,18 nm indicated triplet states completely are unmixed, therefore in a case 1,5-di (p-methoxyphenyl) -3-methylpentazene the pure dissociative state is formed, the curve intercrosses which one the curve of a $S(\pi\pi_1^*)$ - state in a minimum (r = 0,136 nm) potential energy, and $T(\sigma\pi_1^*)$ -state apart r = 0,159 nm, and the crosspoint is higher than bottom of a potential well of a state $T(\sigma\pi_1^*)$ on 1,2 eV.

Thus, initiation of a molecule in $S(\pi\pi_1^*)$-state results in transport of energy on dissociative $T(\pi\sigma^*)$-state , and this process effectively competes to transport of energy to the inferior singlet states, which one is not resonant with $S(\pi\pi_1^*)$-state. Apparently, there is a deflection probability of transport of energy with $T(\pi\sigma^*)$ on $T(\sigma\pi_1^*)$ and S_0-state in points of their cross. As the effect(result), quantum yield of a photodissociation will be to a little bit smaller unity.

As the activated molecule is prompt relax in a dissociative state, the process of dissociation at ambient temperature will be essential to predominate above response of photoisomeric change. At the same time, in the frozen solutions, where the process elongation of dissociative bond inhibited by environmental molecules, probability of relaxation of initiation in $T(\sigma\pi_1^*)$-state will be close to unity.

In this case uniform photochemical process will be isomerization of a molecule, which one and is supervised experimentally.

The similar analysis of potential curves 1,5-diphenyl-3-methylpentazene has shown, what a $T(\pi\sigma^*)$-state concerning a state $S(\pi\pi_1^*)$ is a little bit lower, owing to what the cross of the potential curves is supervised at r = 0,126 nm in a point, which one lies above than minimum $S(\pi\pi_1^*)$-states on 0,48 eV. Therefore, relaxation of initiation $S(\pi\pi_1^*) \rightarrow T(\pi\sigma^*)$ will go to flow past only by a predissociation. Besides there was, what a potential curve mixed $T(\pi\sigma^*) \leftrightarrow T(\sigma\sigma^*)$ -state has a maximum at r = 0,176 nm, in which one energy of highest bottom of this curve on 0,23 eV. The interaction of a dissociative state with inferior by triplet states in crosspoint at 0,159 nm follow-up

will lower probability of a photodissociation of a molecule, which one results in material recession of quantum yield of this response. Nevertheless, in this case crosspoint of the inferior singlet and dissociative states lies above than bottom of the potential curve of a S_1-state all on 0,2 eV, which one will provide padding response of a predissociation with $S(\sigma\pi_1^*)$ (that is S_1) state.

In case of a molecule 1,5-di- (p-nitrophenyl) -3-methylpentazene levels of $S(\pi\pi_1^*)$ and $S(\sigma\pi_1^*)$-states lie very closely to each other, that caused prompt relaxation of electronic initiation between them and essential broadening of intensive absorption band. The curve of a dissociative state $T(\pi\sigma^*)$ cross the curves $S(\pi\pi_1^*)$ and $S(\sigma\pi_1^*)$-states almost in minimums, what should provide high probability of further relaxation of initiation on $T(\pi\sigma^*)$-state. Nevertheless there was, what an energy of electronic system in $T(\pi\sigma^*)$-state at magnification of distance between atoms N_2 and N_3 increases to cross from the curve $T(\sigma\sigma^*)$ by r = 0,2 nm. The barrier of height 0,7 eV is formed, which one essentially brakes process of dissociation. Cross of the configurational curves $T(\pi\sigma^*)$ and $T(\pi\pi_1^*)$ at 0,15 nm results in further relaxation of initiation in $T(\pi\pi_1^*)$-state with further deactivation in a ground state. Therefore, the minor photochemical activity 1,5-di- (p-nitrophenyl)-3-methylpentazene is explained by magnification of height of a barrier, characteristic for dissociative $T(\pi\sigma^*)$ state.

We have tried to describe details of process of dissociation, parsing her(it) how a relation of a constant of velocity of dissociation to the total constants of relaxation of a molecule with triplet $T(\pi\sigma^*)$-state. Thus shall write of velocities constant of dissociation to the shape $k_{dis} = k_0 \exp\left(-\varepsilon/kT\right)$, where ε - activation energy of process of dissociation, and quantity of quantum yield $\varphi = 1/\left[a \cdot \exp\left(\varepsilon/kT\right) + 1\right]$, Where $a = k_{TT}/k_0$, and k_{TT} - constant of a relaxation rate of initiation in $T(\pi\pi_1^*)$-state. Except for the mentioned above activation energies digitized from bottom by the potential curve $T(\pi\sigma^*)$-state, we have taken one more group of energies digitized from energy $T(\pi\sigma^*)$-state apart, which one responds a minimum $S(\pi\pi_1^*)$ - state (accordingly, 0, 0,09 eV and 0,45 eV). The effects(results) of data interpretation have shown, that in coordinates $\ln\left(\dfrac{1}{\varphi} - 1\right)$ - ε dependence rectify with a major error, if for to accept overall height of a barrier, and it is good rectify in the other case. On the other hand has appeared, that the quantity of a declination responds this direct to effective temperature 2100 K at the registration of overall height of a barrier and 1350 K in the other case. It is understandable, that in case of usage of overall height we speak to a barrier about a thermalization of initiation and consequently temperature should be room. Therefore this mechanism not correspond to received(obtained) quantity of effective temperature. In the second case dissociation from a hot state and consequently logically from the very beginning is admitted, that retrieved temperature is peer 1350 K.

Conclusions

- Experimental and theoretical study of spectral and photochemical properties of p-substituted diphenylpentazenes has shown that:
- Pentazenes molecules absorption spectra have an intense long wave-length band due to transition, as well as much weaker short wave-length bands due to a singlet-singlet transition. The $\sigma\rightarrow\pi^*$ and $\sigma\rightarrow\pi_2^*$ quantum transitions are corresponding for weak absorption in short wave spectrum region.
- Asymmetrical isomerization of a pentazene molecule is an effective channel of a relaxation of electronic excitation. Sometimes this one can compete successfully to a photodissociation.
- Pentazene molecules photodissociation proceeds only through molecule symmetry decreasing in a dissociative state; the main dissociative mechanism of the excited methoxy- or nitrosubstituted molecules is the relaxation of an electronic excitation to the dissociative $T(\pi\sigma^*)$-state as well as unsubstituted one through predissociation (electron transition from LUMO to σ^*_{N-N} -MO).

- The high photolysis quantum yield of di-(p-methoxyphenyl)-pentazene means that the dissociative state energy decreases monotonically with the length of dissociating bond enlarging.
- Decreasing of photolysis quantum yield of the unsubstituted and nitrosubstituted pentazenes causes increasing of the dissociative bond length and increasing of the electronic energy of a system in $T(\pi\sigma^*)$-state on 0,23 and 0,70 eV accordingly. It causes a considerable increasing of the contribution of unactive relaxation of initiation into $T(\sigma\pi_1^*)$-state and decreasing of molecule photoactivity.
- Pentazenes molecules dissociation is realized from nonthermalized (hot) $T(n\sigma^*)$-state; a cooling of a solution promotes to initiation thermalization and disappearance of dissociation process as a result.
- A final pentazenes molecules splitting occurs from dissociative $T(\pi\sigma^*)$-state into triazenes, phenyl radicals and nitrogen molecule.

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Abstract

In the paper there are describe results of experimental and theoretical investigations of photochemical processes in solutions of parasubstituted diphenylpentazenes. It is shown that the main photochemical process in liquid solutions is the photodissociation of a molecule due to relaxation of excitation into $T(\pi\sigma^*)$-state. This state is dissociative in a case of metoxysubstituted diphenylpentazene. But with decreasing of a donor-acceptor properties of the substitute high of a potential barrier for dissociation is increased. As a result of dissociation will be formed aryldiimine and triazenyl radicals. In solid (frozen) solutions the photodissociation is inhibited in full and the unique photochemical process will be the asymmetrical photoisomerization.

Анотація

В роботі проведені експериментальні та теоретичні дослідження фотохімічних процесів в розчинах пара-заміщених дифенілпентазенів. Показано, що основним фотохімічним процесом в рідких розчинах є фотодисоціація молекули, яка реалізується внаслідок релаксації збудження в Т($\pi\sigma^*$)-стані молекули. Цей стан виявляється дисоціативним у випадку метоксизаміщеного пентазену. З пониженням донорно-акцепторних властивостей замісника збільшується величина потенціального бар'єра, через який відбувається дисоціація молекули. Внаслідок дисоціації утворюються арилдиімінний та триазенільний радикали. В твердих (заморожених) розчинах фотодисоціація виявляється повністю загальмованою і єдиним фотохімічним процесом виступає несиметрична фотоізомеризація.

Аннотация

В работе описаны результаты экспериментальных и теоретических исследований фотохимических процессов в растворах пара-замещенных дифенилпентазенов. Показано, что основным фотохимическим процессом в жидких растворах является фотодиссоциация молекулы, реализующаяся вследствие релаксации возбуждения в Т($\pi\sigma^*$)-состоянии молекулы. Это состояние оказывается диссоциативным в случае метоксизамещенного пентазена. С понижением донорно-акцепторных свойств заместителя увеличивается величина потенциального барьера, через который совершается диссоциация молекулы. Вследствие диссоциации образуются арилдииминный и триазенильный радикалы. В твердых (замороженных) растворах фотодиссоциация оказывается полностью заторможенной и единственным фотохимическим процессом выступает несимметричная фотоизомеризация.