REGULAR ARTICLE

OPEN ACCESS

Relaxation of Electronic Excitation in Triazide Molecules

P.O. Kondratenko[1,*] ✉ iD, T.M. Sakun[1], Yu.M. Lopatkin[2]

[1] *National Aviation University, 03680 Kyiv, Ukraine*
[2] *Sumy State University, 40007 Sumy, Ukraine*

As a result of studies of the relaxation mechanisms of electronic excitation in triazide molecules: triazidopyrimidine (TAP) and triazido-*S*-triazine (TAT), it was shown that triplet and singlet excited states are states of the $\pi\pi^*$ and $\pi\sigma^*$ type. Both molecules have a flat shape and the same structure of π-molecular orbitals (π-MO). However, they differ significantly in terms of symmetry, which determines the properties of excited states and the relaxation of electrons from excited states. The lowest excited state of both molecules is the binding $T_1(\pi\pi^*)$ state. It is followed in TAP by the dissociative $T_2(\pi\sigma^*)$-state. In TAT, the $T_5(\pi\sigma^*)$ state is dissociative. Both molecules are excited to the singlet $S_4(\pi\pi^*)$ state, from which the molecule relaxes non-equilibrium through intermediate states to the triplet dissociative state. From this state, triazidopyrimidine dissociates with a quantum yield of $\eta = 1.0$, while the quantum yield of triazido-*S*-triazine dissociation will be significantly reduced due to relaxation to the lower triplet states of the same symmetry. Among the singlet states in both molecules, there is a dissociative state, but on the way to dissociation there is an energy barrier capable of slowing down the corresponding process. When the *N-N* bond in both molecules is extended to 1.75 Å, the dissociative state crosses the main S_0 state of the molecule, as a result of which the dissociation product (nitrene) appears in the main triplet state. It is shown that the excitation of a solution of TAP in ethanol increases the quantum yield of photodissociation up to 3.0 due to secondary processes. Such a process is absent in the case of TAT solution.

Keywords: Electronic excitation relaxation, Highly excited states, Dissociative potential surface, Photodissociation of azides.
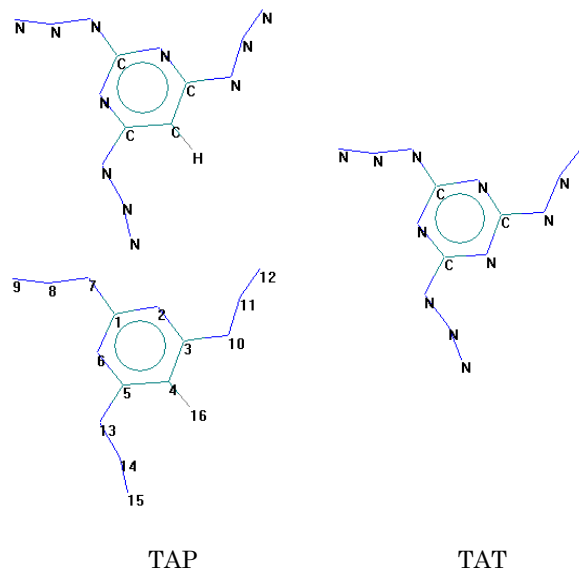
1. INTRODUCTION

In modern science and technology, many molecular compounds are used for the functionalization of nanotubes and nanofibers [1-8], including those from the families of fullerenes and triazides [9-11]. In particular, the ability of azides to create highly reactive intermediates under the influence of light has led to the widespread use of azides in electronics as photoresists [12]. At the same time, the behavior of molecules in the highly excited states and the relaxation of the electronic excitation of molecules is an actual fundamental problem of modern physics and technology.

Until now, very little attention has been paid to the processes of relaxation of the excitation of molecules. It was believed that the laws of photochemistry and, in particular, the fourth law, which states that in the vast majority of photochemical processes that take place in solutions of organic molecules, only the excited state of the molecule in S_1 or T_1 [1], into which the electronic excitation relaxes in a non-equilibrium manner. Subsequently, numerous experimental data appeared, which show that excitation relaxation processes do not interfere with the flow of processes that important for science and practice in highly excited states [8, 13]. In this way, the existence of the quasi-equilibrium relaxation processes of the electronic excitation of molecules was proved.

In this work, the research of quasi-equilibrium processes of electronic relaxation from highly excited states in triazidopyrimidine (TAP) and triazide-*S*-triazine (TAT) molecules is continued:

TAP   TAT

* Correspondence e-mail: pkondrat@ukr.net

2. RESEARCH METHODS OF TAP AND TAT MOLECULES

Experimental studies of relaxation processes of electronic excitation of molecules were carried out in liquid (ethanol) and solid (copolymer of vinylidene chloride, acrylonitrile and methyl methacrylate brand VNM-16) solutions at room temperature. Molecules were excited by monochromatic radiation from a mercury lamp ($\lambda = 313$ nm). The change in optical density during the dissociation of the studied molecule was recorded using a Specord 210 spectrophotometer. The quantum yield of the photodissociation of the studied molecule was found by comparing it with the quantum yield of a known solution (potassium ferrioxalate) [1].

Theoretical studies of the energy structure of TAT and TAP molecules were carried out using the semi-empirical quantum mechanical method of calculating MNDO, created by a group of authors [14, 15] for calculating molecules containing elements of the first and second rows of the periodic table of the chemical elements. This method allows you to calculate the energy structure of the molecule, the shape of the molecular orbitals (MOs) for each state of the molecule, and the strength of the quantum transition oscillator (f). For the calculation in our case, 36 fully filled MOs are taken into account. When performing calculations of excited states, the configurationally interaction between 12 occupied and 12 free MOs is taken into account.

3. ENERGY STRUCTURE OF TAT AND TAP MOLECULES

First of all, we note that the TAT molecule has C_{3h} symmetry, while TAP has C_{1h} symmetry. It follows that in the TAT molecule all three azidogroups are identical, while in TAP they are different. Therefore, the symmetry of the molecule will determine the energy structure of the molecule and the processes of electronic relaxation in it. And this despite the fact that the geometric and π-electronic structure of both molecules is the same. The study of the absorption spectra of these molecules showed that

they really differ significantly both in the position of the absorption bands and in their optical density (Fig. 1).

However, the solutions of both compounds have an absorption band in the region of 313 nm, which made it possible to study the processes of photodissociation of molecules under the same conditions.
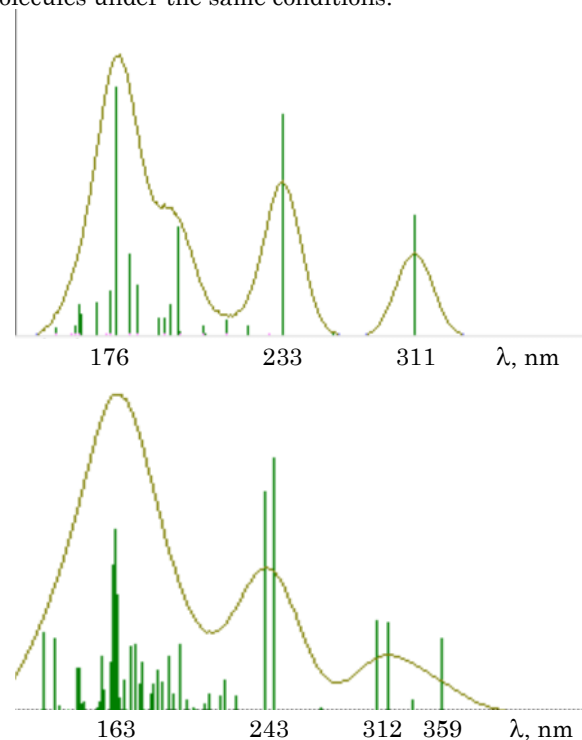

Fig. 1 – Absorption spectra of the alcohol solutions of TAT and TAP (MNDO calculation)

Table 1 shows the results of calculations of the energy structure of TAT and TAP molecules and the absorption spectra corresponding to these structures. The beginning of the countdown to calculate the position of the absorption bands is the binding energy of the electrons localized at 36 MO with the molecular core.

Table 1 – Excitation parameters of the TAP&TAT molecules from the basic geometric configuration

TAP				TAT			
Transition	MO	ΔE, eV	f	Transition	MO	ΔE, eV	f
$T_1(\pi\rightarrow\pi^*)$	36→37,38	2.0004	0	$T_1(\pi\rightarrow\pi^*)$	36→38 35→37 34→42	2.470	0
$T_2(\pi\rightarrow\sigma^*)$	34,35,36→39	2.3089	0	$T_2(\pi\rightarrow\pi^*)$	34→37	2.672	0
$T_4(\pi\rightarrow\pi^*)$	36→42	2.5569	0	$T_3(\pi\rightarrow\pi^*)$	34→38	2.673	0
$T_5(\pi\rightarrow\sigma^*)$	34,36→41	2.6235	0	$T_4(\pi\rightarrow\sigma^*)$	35→39,40 34→40	2.718	0
$S_1(\pi\rightarrow\sigma^*)$	34,35,36→39	2.6251	0.0001	$T_5(\pi\rightarrow\sigma^*)$	36→39 34→41	2.725	0
$S_2(\pi\rightarrow\sigma^*)$	34,36→41	2.9187	0.0001	$S_1(\pi\rightarrow\sigma^*)$	35→40 34→39	3.017	0.0001
$S_3(\pi\rightarrow\sigma^*)$	35,36→40	2.9605	0.0001	$S_2(\pi\rightarrow\sigma^*)$	34→40	3.020	0.0002
$S_4(\pi\rightarrow\pi^*)$	36→37	3.4896	0.2286	$S_3(\pi\rightarrow\sigma^*)$	36→39 34→41	3.023	0.0000
$S_5(\pi\rightarrow\pi^*)$	36→38	3.6922	0.0458	$S_4(\pi\rightarrow\pi^*)$	34→37	3.983	0.3921

Table 1 shows that the symmetry of the molecule determines the fact that the energy levels of the excited states of TAT appear in triplets. At the same time, the three lower triplet quantum transitions are represented by electronic excitation between π-MO and π^*-MO, the next three transitions are between π-MO and σ^*-MO. As for singlet quantum transitions, in this case the three lower transitions correspond to the excitation of electrons between the π-MO and σ^*-MO. At the same time, in accordance with the symmetry of the molecule, the specified σ^*-MOs are delocalized mainly on all azido groups, which ensures the photochemical activity of molecules from only one $T(\pi\sigma^*)$ state. At the same time, one of these orbitals must be dissociative. A decrease in the symmetry of the molecule due to an increase in the distance between nitrogen atoms No 13 and 14 will cause a corresponding transformation of the σ^*-MO and a decrease in the energy of the corresponding excited state.

As can be seen from Table 1, the excitation of TAT and TAP molecules occurs only in the $S_4(\pi \rightarrow \pi^*)$ state, after which the electronic excitation relaxes to the triplet dissociative state.
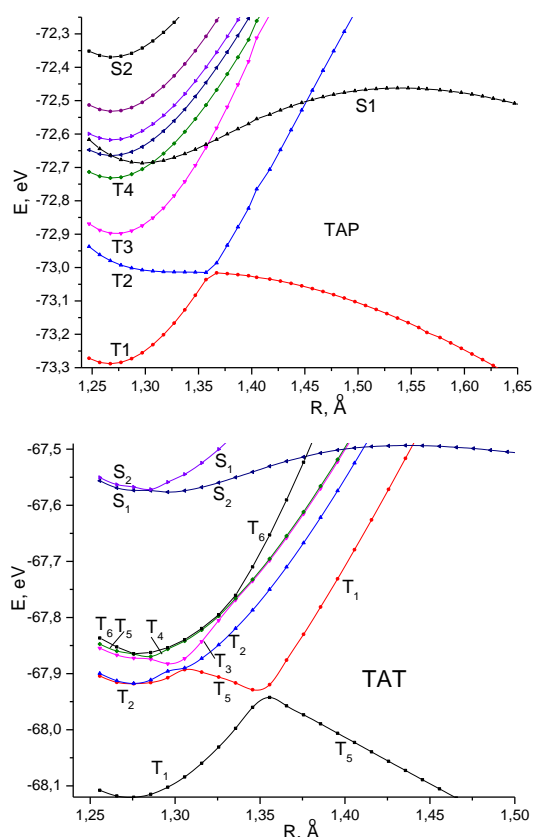

Fig. 2 – Energy structure of TAP and TAT depending on the length of the N(13)-N(14) bond

It was shown in [1, 5] that the processes of dissociation of a molecule into fragments are possible exclusively from $\pi\sigma^*$ states. Therefore, one of the T_4, T_5 or T_6 states will be responsible for the dissociation of the azidogroup upon excitation of the TAT molecule. The calculation showed that the T_5 state is dissociative. When the N-N bond is elongated, this state intersects with other triplet states (Fig. 2), as a result of which relaxation of the excitation to the T_1 state is possible, and the quantum yield of molecular dissociation will drop significantly. Experimental studies have shown that the quantum yield of photodissociation of the N-N bond in ethanol is 0.30, and in a solid polymer solution it is 0.17. Therefore, the channel of non-radiative relaxation of electronic excitation in TAT is quite significant.

Analogous studies of singlet quantum transitions in the TAT molecule showed that the first three excited states correspond to the excitation of electrons between the π-MO and σ^*-MO and only the following quantum transitions are due to the electronic excitation between the π-MO and π^*-MO. Since the π-MO and σ^*-MO practically do not overlap, this leads to a very small value of the corresponding oscillator strength f (Table 1) and the absence of a noticeable absorption band in the long-wavelength part of the absorption spectrum of the compound solution. However, it is precisely these quantum transitions that can ensure the dissociation of the molecule.

If one of the first three singlet states is responsible for the dissociation of the molecule, it can be expected that the quantum yield of such a process can be close to unity. The study showed that the S_2 state is dissociative. However, in this case, a barrier with a height of 0.083 eV stands on the way to increasing the length of the N-N bond. In addition, there is an intersection of the S_2 state with the triplet states T_1, T_2, T_3, T_4 and T_6 (Fig. 2), which will further reduce the probability of TAT dissociation from the S_2 state.

Since the symmetry of the molecule decreases during the elongation of the N-N bond, the interaction between the T_5 state and the lower triplet states is manifested, as a result of which energy corresponding surfaces are broken at the crossing points. However, in the conditions of non-equilibrium relaxation of the electronic excitation, this gap will not affect the process of dissociation of the N-N bond.

With further lengthening of the N-N bond to 1.75 Å, the energy surface of the T_5 state intersects with the main S_0 state. Therefore, upon dissociation of the N-N bond, a product with a ground triplet state will be formed. This creates a nitrene – a molecule with a single C-N bond and two unbonded molecular orbitals (MOs) localized on the nitrogen atom. One electron is localized on these MOs, as a result of which the ground state of the nitrene is the triplet state.

Now, for comparison, consider the TAP molecule. The replacement of the N atom by C causes a decrease in the symmetry of the molecule to C_{1h}. And this, in turn of, will change the energies of quantum transitions and their symmetry (Table 1). It is important that in this case all σ^*-MOs are each localized on one azidogroup. And this will contribute to the fact that each of the three triplet states will be dissociative. However, they correspond to different energies of the excited state. Moreover, immediately after the $T_1(\pi \rightarrow \pi^*)$ state is the $T_2(\pi \rightarrow \sigma^*)$ state (Table 1). This state corresponds to the azidogroup localized near the carbon atom at point 5. Therefore, the second triplet quantum transition turned out to be dissociative. Only the $T_1(\pi \rightarrow \pi^*)$ state is located below this state. Since the nature of these excited states

is different, at their intersection in the process of dissociation, there is no internal conversion between them.

As a result, the localization of excitation on the $T_2(\pi \to \sigma^*)$ state will lead to the dissociation of molecules with a large quantum yield. The other two triplet $T(\pi \to \sigma^*)$ states are also dissociative, but in the process of dissociation of the TAP molecule, these states intersect not only with $T(\pi \to \pi^*)$ states, but also with $T(\pi \to \sigma^*)$- states. This will cause relaxation processes of the electronic excitation to the $T_2(\pi \to \sigma^*)$ state. Experimental studies show that the quantum yield of TAP photodissociation in solid polymer solutions reaches 1.0.

It turned out that the first three singlet excited states of TAP are caused by $\pi \to \sigma^*$ quantum transitions. Moreover, the $S_1(\pi \to \sigma^*)$ state turned out to be dissociative. As in the case of TAT, there is a potential barrier of 0.225 eV on the way to the dissociation of the N-N bond in the TAP molecule. This barrier will completely exclude the possibility of dissociation of the molecule both at room and at low temperatures. Therefore, the only dissociative state will remain the $T_2(\pi \to \sigma^*)$ state.

Now we will consider the possible mechanisms of TAP dissociation processes in a liquid solution (ethanol). The fact is that the quantum yield of TAP in ethanol reaches 3.0. And it is not the dissociation of all three azidogroups in one molecule, but the dissociation of one bond in three different molecules. This conclusion can be made on the basis that the absorption spectrum of the product of TAP transformation (diazidopyrimidineamine) is different from the absorption spectrum of TAP, and the study of photodissociation of TAP was carried out by recording the optical density of the long-wavelength absorption band of TAP.

We conducted a study of the interaction between ethanol molecules and TAP in the process of nitrene formation. At the same time, it turned out that in the absence of other interactions, the nitrene pulls the hydrogen atom away from the carbon atom bound to the OH group in the ethanol molecule, or is inserted into the same C-H bond. The formed H_3C-CH·-OH radical does not interact with the TAP molecule.

Further studies showed that the ethanol molecule is able to form a hydrogen bond with nitrogen atom No 13. The energy of this bond is only 0.071 eV. However, this energy exceeds the thermal energy at room temperature (0.025 eV), which ensures the existence of the complex due to the hydrogen bond for a certain time. Therefore, during the dissociation of the N-N bond in the TAP molecule bound by a hydrogen bond to two ethanol molecules, hydrogen atoms are transferred from the OH groups of these molecules to the nitrene molecule. At the same time, two H_3C-CH_2-O· radicals are formed, each of which showed great activity when interacts with another TAP molecule. This activity led to the release of a nitrogen molecule from the azidogroup, and the nitrogen atom No 13 bonded with the H_3C-CH_2-O· radical into a

strong molecule.

In this way, two processes were outlined. In the primary process, the photodissociation of the N-N bond occurs in the azidogroup attached to atom No 5 in the TAP molecule, and in the secondary process, after the transfer of hydrogen atoms in the ethanol-TAP molecule complex, the formed radical H_3C-CH_2-O· interacts with another TAP molecule, and it leads to the rearrangement of bonds and the release of a nitrogen molecule from the azidogroup located near atom No 5 in the TAP molecule. As a result, the resulting quantum yield of TAP photolysis in ethanol reaches 3.0.

4. CONCLUSIONS

Based on the study of the electronic relaxation processes in TAP and TAT molecules and comparison of the identified processes and properties of these compounds, the following conclusions were made.

1. The C_{3h} symmetry of the TAT molecule caused the delocalization of σ^*-MO on all three azidogroups at once. This caused the fact that only the $T_5(\pi \to \sigma^*)$ state was dissociative.

2. Since in the process of elongation of the N-N bond in the azidogroup, this state intersects with the lower triplet states, an effective excitation relaxation channel to the $T_1(\pi \to \pi^*)$ state is opened, as a result of which the quantum yield of photodissociation of the TAT molecule decreases in ethanol to 0.3. An additional reduction of the quantum yield to 0.17 is observed in a solid polymer solution due to steric hindrances.

3. The TAP molecule, similar to the TAT molecule, has a flat geometric structure and the same π–electron structure. However, the symmetry of the molecule is lowered to C_{1h}, as a result of which there is a significant change in the energy structure and relaxation mechanisms of electronic excitation.

4. In the TAP molecule, the second triplet state is the dissociative $T_2(\pi \to \sigma^*)$ state. Since the first triplet state is the $T_1(\pi \to \pi^*)$ state, the processes of non-radiative relaxation of electronic excitation will be prohibited, as a result of which the quantum yield of the photodissociation of the TAP molecule will be equal to 1.0 in solid polymer solutions. The same will be the quantum yield of the primary process in the ethanol solution.

5. Experimental studies of photodissociation of TAP solution in ethanol showed that in this case the quantum yield increased to 3.0 due to secondary processes. Secondary processes are caused primarily by the formation of a hydrogen bond between the OH group in two ethanol molecules and nitrogen atom No 13 in the TAP molecule. This causes the transfer of hydrogen atoms from OH groups to nitrene with the formation of active radicals H_3C-CH_2-O·, capable of interacting with other TAP molecules and causing rearrangement of bonds with the release of a nitrogen molecule from the azidogroup.

REFERENCES

1. P.O. Kondratenko, *Fotokhimichna diya svitla* (VTS Kyyivskyi Universytet: Kyiv: 2005).
2. M. Hircher, M. Becher, *J. Nanosci. Nanotechnol.* **3** No 1-2, 3 (2003).
3. R.G. Ding, G.Q. Lu, Z.F. Yan, M.A Wilson, *J. Nanosci. Nanotechnol.* **1** No 1, 7 (2001).
4. P.A. Kondratenko, Yu.M. Lopatkin, T.N. Sakun, *Photoelectronics* **22**, 117 (2013).

5. P.O. Kondratenko, Yu.M. Lopatkin, T.N. Sakun, _J. Nano-Electron. Phys._ **4** No 2, 02017 (2012).
6. S. Farhat, B.Weinberger, F.D. Lamari, T. Izouyar, L. Noe, M. Monthioux, _J. Nanosci. Nanotechnol._ **7** No 10, 3537 (2007).
7. A. Lan, A. Mukasyan, _J. Phys. Chem. B_ **109** No 33, 16011 (2005).
8. P.O. Kondratenko, Yu.M. Lopatkin, T.M. Sakun, _J. Nano-Electron. Phys._ **12** No 5, 05002 (2020).
9. Manish Gaur, Charu Misra, Awadh Bihari Yadav, Shiv Swaroop, Fionn Ó Maolmhuaidh, Mikhael Bechelany, Ahmed Barhoum, _Materials_ **14** No 20, 5978 (2021).
10. María Isabel Lucío, Federica Pichler, José Ramón Ramírez, Antonio de la Hoz, Ana Sánchez-Migallón, Caroline Hadad, Mildred Quintana, Angela Giulani, Maria Victoria Bracamonte, Jose L.G. Fierro, Claudio Tavagnacco, María Antonia Herrero, Maurizio Prato, Ester Vázquez, _Chemistry_ **22** No 26, 8879 (2016).
11. Gang Ke, _Carbohydrate Polymers_ **79** No 3, 775 (2010).
12. Marvin Schock, Stefan Bräse, _Molecules_ **25** No 4, 1009 (2020).
13. P.O. Kondratenko, Yu.M. Lopatkin, T.M. Sakun, _Phys. Chem. Solid State_ **8** No 1, 100 (2007).
14. Michael J. S. Dewar, Walter Thiel, _J. Am. Chem. Soc._ **99** No 15, 4899 (1977).
15. Walter Thiel, _WIREs Comput. Molec. Sci._ **4** No 2 145 (2014).

Релаксація електронного збудження в молекулах триазидів

П.О. Кондратенко[1], Т.М. Сакун[1], Ю.М. Лопаткін[2]

[1] _Національний авіаційний університет, 03680 Київ, Україна_
[2] _Сумський державний університет, 40007 Суми, Україна_

В результаті проведених досліджень механізмів релаксації електронного збудження в молекулах триазидів: триазидопірімідину (ТАП) і триазидо-S-триазину (ТАТ) показано, що триплетними і синглетними збудженими станами є стани типу $\pi\pi^*$ і $\pi\sigma^*$. Обидві молекули мають плоску форму і однакову структуру π-молекулярних орбіталей (π-МО). Проте, вони суттєво відрізняються за симетрією, яка й визначає властивості збуджених станів і релаксацію електронів зі збуджених станів. Нижнім збудженим станом в обох молекулах є зв'язуючий $T_1(\pi\pi^*)$-стан. За ним в ТАП слідує дисоціативний $T_2(\pi\sigma^*)$-стан. В ТАТ дисоціативним є $T_5(\pi\sigma^*)$- стан. Збудження обох молекул відбувається в синглетний $S_4(\pi\pi^*)$-стан, з якого молекула релаксує нерівноважним чином через проміжні стани до триплетного дисоціативного стану. З цього стану відбувається дисоціація ТАП з квантовим виходом $\eta = 1,0$, в той час як квантовий вихід дисоціації ТАТ буде суттєво пониженим внаслідок релаксації до нижніх триплетних станів тієї ж симетрії. Серед синглетних станів в обох молекулах є дисоціативний стан, проте на шляху до дисоціації існує енергетичний бар'єр, здатний загальмувати відповідний процес. При видовженні N-N- зв'язку в обох молекулах до 1,75 Å дисоціативний стан перетинає основний S_0-стан молекули, внаслідок чого продукт дисоціації (нітрен) виявляється в основному триплетному стані. Показано, що збудження розчину ТАП в етанолі підвищує квантовий вихід фотодисоціації до 3,0 за рахунок вторинних процесів. Такий процес відсутній у випадку розчину ТАТ.

Ключові слова: Релаксація електронного збудження, Високозбуджені стани, Дисоціативна потенціальна поверхня, Фотодисоціація азидів.