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Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electronic Excitation Energy Transfer in DNA. Nature of Triplet Excitations Capturing Centers

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Version of record first published: 22 Sep 2010

To cite this article: Valeriy M. Yashchuk, Vladislav Yu. Kudrya, Mykhaylo Yu. Losytskyy, Igor Ya. Dubey & Hiroaki Suga (2007): Electronic Excitation Energy Transfer in DNA. Nature of Triplet Excitations Capturing Centers, Molecular Crystals and Liquid Crystals, 467:1, 311-323

To link to this article: http://dx.doi.org/10.1080/15421400701224751

Mol. Cryst. Liq. Cryst., Vol. 467, pp. 311–323, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701224751

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Spectral properties, energy structure, and electronic processes in DNA, poly $(dAdT)_2$, d(CCCGGGTTTAAA), d(ATC), d(AT), dGMP, dAMP, dCMP, dTMP were studied. The DNA lowest excited electronic singlet and triplet levels are connected with guanine and adenine bases, correspondingly. The DNA fluorescence is close to a linear combination of the guanine and cytidine emissions and connected, to a greater extent, with the singlet energy transfer to these bases. The origin of the DNA phosphorescence is associated with AT-sequences that are traps of triplet excitations in DNA. The triplet energy transfer to these centers and adenine bases (that are most photostable) leads to the DNA self-protection against a damage induced by electronic excitations of DNA.

We are grateful to Prof. Paras N. Prasad, Prof. Dmytro M. Govorun, Dr. Tymish Yu. Ohulchanskyy, Prof. Petro Doroshenko, Dr. Volodymyr P. Vorobyov, and Prof. Volodymyr I. Melnik for their ideas and help.

This work was supported in part by STCU (Project No 3104) and the Ministry of Education and Science of Ukraine (Project No. M/229-2004).

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Keywords: DNA, energy structure, energy transfer, triplet states

1. INTRODUCTION

In non-conjugated polymers and copolymers, the π-electron systems are localized in separate groups–so-called chromophores (e.g., polysterene, polyvinylnaphthalene, polyvinylcarbazole). Such important biopolymer macromolecules as DNA and RNA belong to this type of macromolecules [1]. It is known [2–11] that the electronic energy structure of these macromolecules is connected mainly with individual properties of their π-electron-containing groups. The later gives the ground to evaluate the positions of energy levels of macromolecules using the spectroscopic data for compounds that are the models of separate chromophore-containing macromolecules. Approximately such an approach was applied in early works [1,12–19]. In [18], the related positions of the DNA bases (A,T,G,C) singlet (S) and triplet (T) energy levels were presented as following: $S_A > S_T > S_G > S_C$, $T_C > T_G > T_A > T_T$.

It appeared that our data on the DNA damage (presented in this article and in [20]) do not agree with the triplet levels positions obtained in [18]. It is necessary to say that there were some reasons for that. The model compounds used in [18] were more suitable for RNA than for DNA. The evaluation of the spectral position of the thymidine phosphorescence spectrum blue edge in this article as compared with the same for adenosine is not so clear due to the low intensity and the smooth short-wave shape of the thymidine phosphorescence spectrum at $T = 77\,K$. The nature of the DNA luminescence, especially of its phosphorescence, was not described clearly in early works. Papers [22–25,37–43] following [1,12–19] added no new essential information concerning positions of the DNA energy levels and the nature of excitations intrinsic traps (especially triplet traps and their connection with the DNA damage occurring through the electronic excited sites).

In the present article, the attempt to obtain a clearer picture for the DNA electronic energy structure, electronic excitation energy transfer, the nature of excitation capturing centers, and their effect on the DNA damage has been done using low-molecular compounds, being DNA's elementary fragments, which is more correct and more suitable for DNA. In addition, some specially designed compounds containing the nucleotides π-electron systems were applied to explain the DNA phosphorescence origin. For a more exact evaluation of the triplet levels positions, the spectral measurements at $T = 4.2\,K$ were conducted.

2. EXPERIMENTAL

The total DNA from chicken erythrocytes and poly(dAdT)$_2$ polynucleotide were purchased from Sigma. The model compounds - monophosphates of 5′-deoxyadenosine (dAMP), 5′-deoxythymidine (dTMP), 5′-deoxyaguanosine (dGMP), 5′-deoxycytidine (dCMP),- and trimer d(ATC) were obtained from the Institute of Molecular Biology and Genetics (IMBG) of the NAS of Ukraine. These compounds (contrary to rAMP, rGMP and rCMP used in [18]) are more correct models of the DNA elementary links. The compounds d(CCCGGGTTTAAA), d(CCCCCCCCCCCC), d(GGGGGGGGG GGG), d(TTTTTTTTTTTT) and d(AAAAAAAAAAAA) were synthesized in SUNY. The steady-state fluorescence measurements were performed with Hitachi 850 and MPF-4 spectrofluorometers; the absorption spectra were recorded on a Specord UV-VIS spectrophotometer. The phosphorescence spectra were obtained using a laboratory-designed equipment. The spectral measurements were carried out at 4.2 K, 77 K, and ambient temperatures.

3. RESULTS AND DISCUSSION

3.1. Singlet Electronic Sites of DNA

In our opinion, the first fundamental investigation of the intramolecular singlet energy transfer and trapping of singlet excitations by the intrachain traps (methylated guanine bases) in DNA was performed in [40]. It was shown the energy of at least one of three photons absorbed by the normal bases was trapped by chemically modified bases, the singlet excitation energy being transferred for only 1–2 bases at ambient temperatures. The fact of the intramolecular singlet excitation transfer was also observed in synthetic low-molecular analogs of DNA (decamers) with chemically attached 2-aminopurine groups [37,38]. In [44], it was suggested that, in poly(dG-dC)-poly(dG-dC) polynucleotide, the excitation energy is transferred from the lower-energy electronic state of guanine to cytosine before the vibronic relaxation is established. At the same time, the fluorescence spectrum of poly(dA-dT)-poly(dA-dT) was found to consist of (1) the thymine fluorescence and (2) the emission of A-T excimers [45]. Hence, it was shown that the singlet excitation energy transfer in the DNA exists at room temperature, but excitations are spread for only short distances. Nevertheless, such short-distance energy transfer should have significant influence on the photoreactions in DNA.

As was shown in a number of works (see, for example, [1,20,21]), the electronic absorption spectrum of DNA is close to the additive sum of

the spectra of the corresponding nucleotides, which is typical of non-conjugated π-electron-containing polymers [2,11,26–28]. Our experimental data confirm this (Fig. 1). Thus, the nucleotides are practically independent absorbing centers in the DNA macromolecule (as well as in d(CCCGGGTTTAAA)), and the electronic processes in it start from initially excited DNA bases. From the other point of view (based mainly on some computer simulations), the excitations in the DNA can be delocalized initially at least among two neighbor bases [41,42]. It is worth to note that the absorption spectra of DNA and nucleotides at 77 K [18] are generally similar to those observed at room temperature.

The absorption and fluorescence spectra obtained in our experiments (Fig. 2) give the values of singlet level energies (Fig. 5) (since the displacement of the first singlet excited level is obtained by the intersection of the absorption and fluorescence spectra curves normalized on the first maxima, the full shape of the absorption spectrum curve is shown by a dotted line additionally for dGMP, Fig. 2a) [29]. As follows from these data, the energy values for singlet electronic levels decrease in the order: $S_A > S_T > S_C > S_G$ (Fig. 5). It is worth to note that the difference between the C and G energy levels is small as compared with the value of kT at ambient temperatures.

Unlike absorption, the fluorescence spectrum of DNA (as well as synthetic compound d(CCCGGGTTTAAA)) cannot be fitted by the sum of the spectra of the corresponding nucleotides. This fact can be explained

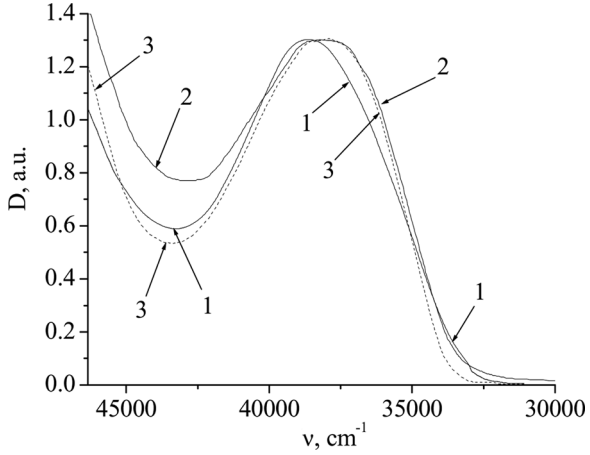

FIGURE 1 Optical absorption spectra of: DNA (1), d(CCCGGGTTTAAA) (2) and a linear combination of dGMP, dCMP, dAMP, and dTMP spectra (3). Water solutions, $C = 10^{-4}$ M.

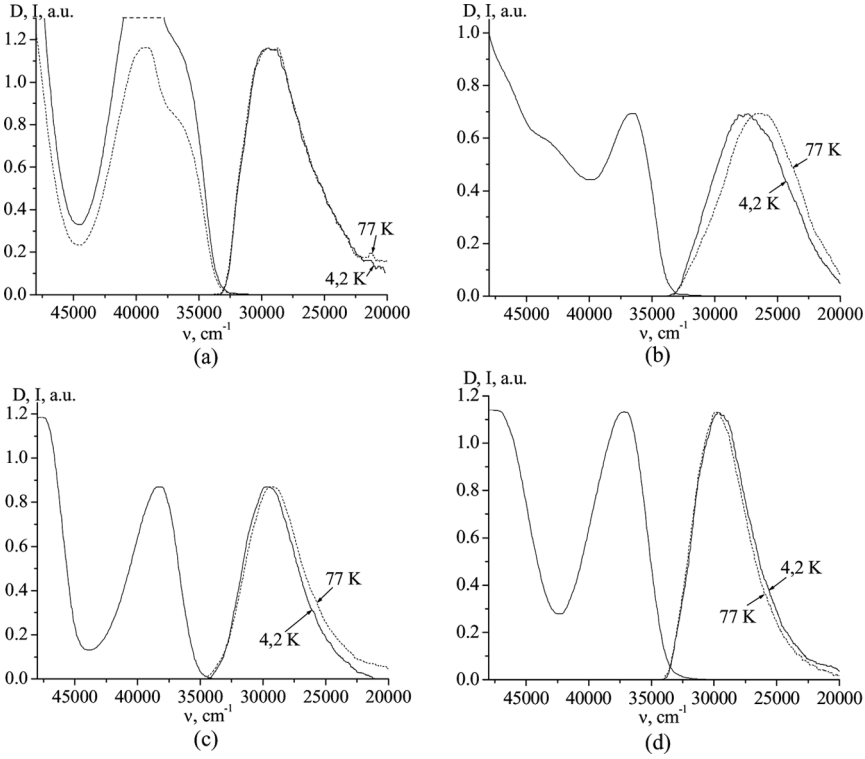

FIGURE 2 Optical absorption (1) and fluorescence spectra at T = 4.2 K (2) and T = 77 K (3) of: dGMP (a), dCMP (b), dAMP (c), and dTMP (d). Water solutions, C = 10^{-4} M, excitation at 260 nm.

(as in the case of synthetic non-conjugated polymers [10,11,27,28]) by the existence of singlet excitation energy transfers to intramolecular traps in the DNA macromolecule. In the native DNA, the G-sites with the lowest energy can play a role of these traps. But the energy of C- sites is very close to that of G-sites (near kT at 77 K). The exciplexes between C- and G-bases can be formed, but we cannot exclude the formation of other types of traps [22,30]. In addition, according to our data [20], the significant part of singlet excitations in the pure DNA can be deactivated by the emission from C- and G- sites (the DNA fluorescence spectrum is close to a linear combination of the dCMP and dGMP fluorescence spectra taking into account their quantum yields and the possible transfer from G-base to C-base in a complementary pair by the Förster mechanism, see Fig. 3). The intra-DNA singlet excitation energy transfer could start from C and G bases after the localization of excitations

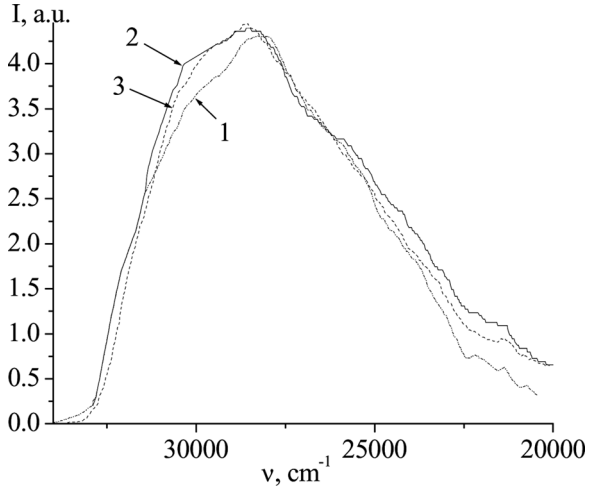

FIGURE 3 Fluorescence spectra at $T = 77\,K$ of: DNA (1), d(CCCGGG TTTAAA) (2) and a linear combination of the dCMP and dGMP spectra (3). Water solutions, $C = 10^{-4}\,M$, excitation at 260 nm.

on them. At any rate, the singlet excitations can spread along the DNA macromolecule at least at a distance that corresponds to the length of four bases at $T = 77\,K$.

Our previous data [21] proves the existence of the singlet energy transfer from the DNA bases to intercalated cyanine dyes, but the resulting spreading length of singlet excitons does not exceed the length of a few DNA base pairs.

3.2. Phosphorescence of DNA and Nucleotides. System of Triplet Electronic Energy Levels

DNA manifests the phosphorescence emission at low temperatures. Only a few investigations [12,14–19,31] were devoted to the phosphorescence of DNA and nucleotides and its quantum yields and life time [31]. Namely, the phosphorescence spectra give the possibility to evaluate the position of the triplet levels of the DNA bases. These levels play an important role in processes caused by the appearance of the excitation in the macromolecule due to: photon absorption, interaction with α, β, γ-radiation, or another action.

The phosphorescence spectra of dAMP, dTMP, dGMP, and dCMP at 77 and 4.2 K are presented in Figure 4. All of them are in the range of 350÷550 nm. The dAMP and dGMP phosphorescence spectra are more

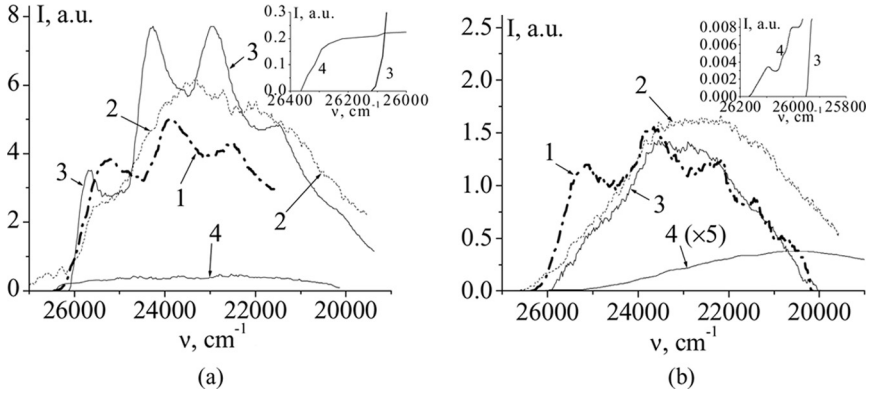

FIGURE 4 Phosphorescence spectra at T = 4.2 K (a) and T = 77 K (b) of: dGMP (1), dCMP (2), dAMP (3), and dTMP (4). Water solutions, C = 10^{-4} M, excitation at 260 nm.

structured and more intense; dCMP and dTMP manifest the phosphorescence with practically unstructured spectra. The spectra obtained at 77 K look like those obtained in [19]. The change from 77 to 4.2 K leads to increasing the phosphorescence intensity and structuring the spectra. The phosphorescence spectra of DNA and model compounds at 4.2 K were obtained by us for the first time.

The position of the blue edge of the phosphorescence spectra allows the evaluation of a position of triplet electronic levels (0–0 transition) [29]. The positions of the triplet levels T_1 determined from the blue edges of dAMP, dTMP, dGMP, and dCMP are given in Figure 5. We consider that this system of energy levels can be examined as the system of the DNA base triplet levels. Our data show that the triplet level of the adenine base is lowest in DNA contrary to the results obtained in [18,19].

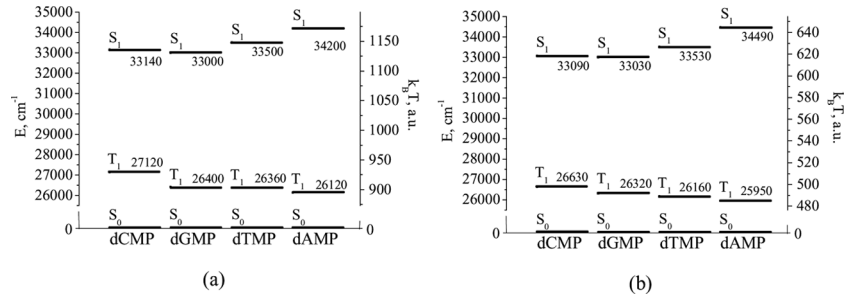

FIGURE 5 Singlet and triplet energy levels of the DNA bases at T = 4.2 K (a) and T = 77 K (b).

It follows from the data presented above in Figure 5 that there are some red shifts of triplet level positions with the temperature increasing from 4.2 to 77 K. For dTMP and dAMP, these shifts are ~140 and 170 cm^{-1}, the signs of temperature shifts being the same.

3.3. Triplet Excitation Energy Transfer in the DNA Macromolecule. Nature of the DNA Phosphorescence

Possibly, the intramolecular triplet excitation energy transfer in the DNA macromolecule was observed firstly by Berson and Isenberg in 1964 [12]. The average value of the triplet excitations spreading length was obtained to be close to 20 base pairs along the DNA chain. There were no other experimental works of such a type up to now, though there were some articles that prove directly [33] or indirectly [32] the existence of the triplet excitation energy transfer in DNA.

The triplet energy transfer along the DNA macromolecule should lead to the localization of migrating triplet excitations on the DNA bases with the lowest triplet energy levels. As was shown above, the triplet level of A base is the lowest. So, it seems that the phosphorescence spectrum of DNA must be close to the dAMP phosphorescence spectrum. But this is not the case. The DNA phosphorescence spectrum (Fig. 6) does not look like any of the bases phosphorescence spectra. In [19], it was supposed that the DNA phosphorescence spectrum is

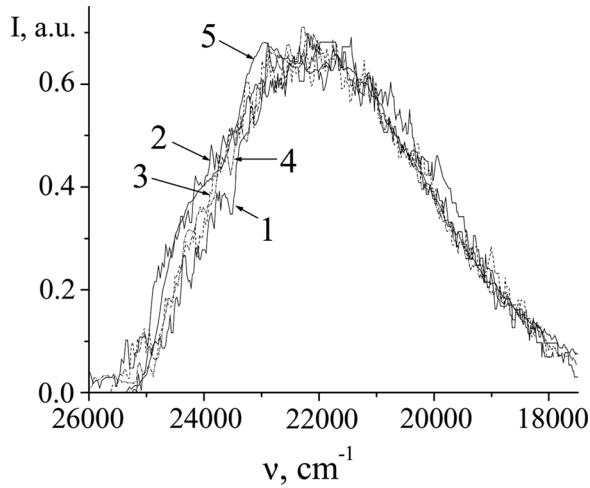

FIGURE 6 Phosphorescence spectra at T = 77 K of: DNA (1), d(CCCGGGTTTAAA) (2), poly(dAdT)$_2$ (3), d(ATC) (4), and d(AT) (5). Water solutions, C = 10^{-4} M, excitation at 300 nm.

originated from the ionized T-base π-electron system. Our supposition is that the localization of the triplet excitations on the adenine groups takes place at the beginning of the processes, and then a triplet exciplex or another complex forms between adenine and a neighbor base of the same DNA chain.

To check the above-proposed pathway of the triplet excitation transfer along the DNA-macromolecule and the origin of the DNA phosphorescence emission centers, a special oligomer compound, d(CCCG GGTTTAAA), was designed and synthesized. The absorption spectrum of d(CCCGGGTTTAAA) is close to the sum of the spectra of G,C,T,A-model compounds (dGMP, dCMP, dTMP, and dAMP). It follows from the schemes of energy levels (Fig. 5) that the disposition of triplet levels in the oligomer d(CCCGGGTTTAAA) favors the triplet excitation energy transfer from CCC-links to AAA-links. This means that the excitation of this synthetic compound has to result in the phosphorescence of A-cells. But the experiments show that triplet excitations are not deactivated from the A bases, because there is a big difference between the phosphorescence spectra of dAMP and the model oligomer. In addition, the phosphorescence spectrum of the oligomer does not correspond to the sum of dCMP, dGMP, dTMP, and dAMP phosphorescence spectra, but it is very close to the DNA phosphorescence spectrum. The hypothesis that triplet excitations are localized at the excimer-like traps was checked by using d(CCCCCCCCCCCC), d(GGGGGGGGGGGG), d(TTTTTTTTTTTT), and d(AAAAAAAAAAAA). The phosphorescence spectra of these compounds (Fig. 7) are rather different from the phosphorescence spectra of d(CCCGGGTTTAAA) and DNA (Fig. 6). This means that CCC, GGG, TTT, and AAA-sequences in the d(CCCGGGTTTAAA) oligomer molecule are not the trapping sites for triplet excitations. But what is then? Probably, the boundary pairs (between triads), e.g, AT, can be traps of triplet excitons.

Indeed, the investigations of the poly$(dAdT)_2$, d(ATC), and d(AT) (specially designed and synthesized) luminescence have shown that the phosphorescence spectra of these compounds are very close to the d(CCCGGGTTTAAA) oligomer phosphorescence spectrum. Moreover, the shapes of all these spectra are similar to the shape of the DNA phosphorescence spectrum (Fig. 6).

So, our conclusion is that the intramolecular AT sequences in the investigated model compounds, as well as the AT sequences in DNA, are acting as the traps for triplet migrating excitations. The average value of the relative number of AT sequences in the chicken DNA studied in this work is about 1/16. This means that the resulting average displacement of triplet excitons in DNA equals the distance that corresponds at least to the length of sixteen base pairs.

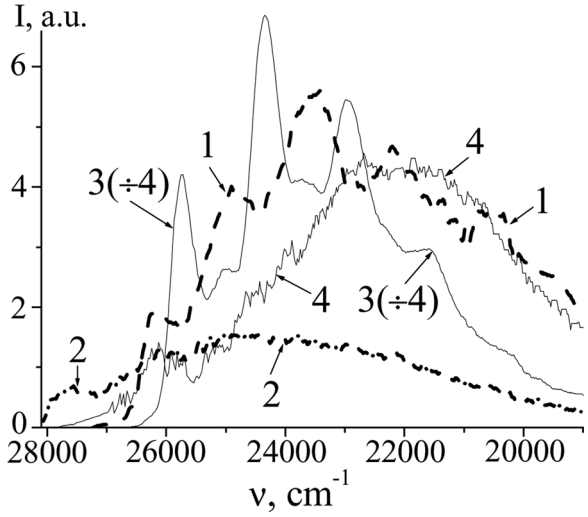

FIGURE 7 Phosphorescence spectra at T = 77 K of the water solutions of oligomers: d(GGGGGGGGGGGG) (1), d(CCCCCCCCCCCC) (2), d(AAAAAA AAAAAA) (3), d(TTTTTTTTTTTT) (4).

This value is in agreement with Berson's and Isenberg's results (20 base pairs) [12].

The results presented above prove that mobile triplet excitations in DNA and oligomer d(CCCGGGTTTAAA) after the previous relaxation to A-bases are captured by the traps formed in AT-sequences. So the chemical reactions initiated by triplet excitations should start from A-bases or AT-sequences that, according to our investigations, are rather photostable. It is clear that some part of excitations causes the DNA damage before their capturing on A- or AT-traps. The data on the UV-induced damage of nucleotide-containing model compounds additionally prove our suggestions.

4. UV-Damage of DNA

The additional information on the identification of the triplet electronic excitation localization sites in DNA was obtained using photochemical reactions and assuming that excited triplet sites favor these processes. It is known that UV-irradiation destroys the DNA bases [20,32,34,35,43]. It becomes apparent in a decrease of the DNA absorption near 260 nm and some changes in the short-wave part of the DNA spectra. We have carried out the comparative investigations of the UV-damage of DNA, model base compounds (dAMP,

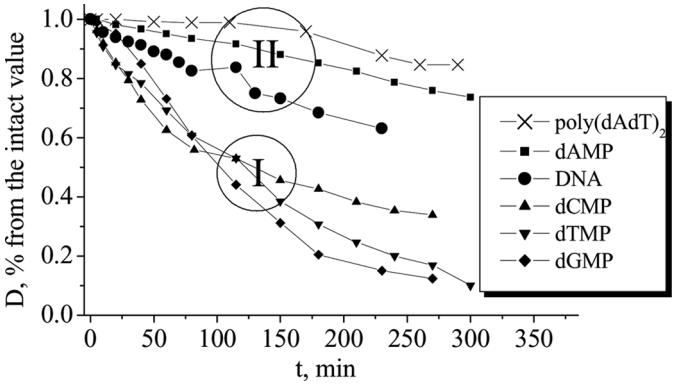

FIGURE 8 Dependence of the optical density in the absorption maximum of DNA, poly(dAdT)$_2$, and nucleotides on the time of UV-irradiation. T = 293 K. Water solutions, concentrations of about 7×10^{-5} M. Irradiation wavelength of 253 nm.

dTMP, dCMP, dGMP), and poly (dAdT)$_2$. In Figure 8, the dependences of the DNA and model compounds absorption at 260 nm on the time of UV-exposure are presented. As follows from this figure, the initial decrease rate of absorption for dTMP, dCMP, and dGMP (**I**, Fig. 8) is essentially higher than that for dAMP (**II**, Fig. 8). This is in agreement with the data obtained in [35,36]. It is known that the adenine base in DNA is the most stable relative to other bases [36]. According to our data, the rates of decrease in the absorption of DNA and dAMP (**II**, Fig. 8) under UV-irradiation are more close. This proves our suggestion that the main part of triplet excitations is initially localized on the adenine bases. On the other hand, the phosphorescence data show the localization of mobile triplet excitations on the AT-base sequences. In this case, the localization of triplet excitations in the AT-sequences must lead to similar initial damage rates for DNA and poly(dAdT)$_2$. Indeed, the rate of change in the absorbance of DNA upon UV-irradiation is closer to the rate of the corresponding change for dAMP and poly(dAdT)$_2$. Slightly faster changes for DNA compared with dAMP and poly(dAdT)$_2$ are connected, in our opinion, with the localization of some part of triplet excitations on the other DNA-bases, for which the UV-induced damage rate is essentially higher [20]. So, the system of the DNA electronic levels is organized in such a way (see Fig. 5) that the processes of electronic excitation energy transfer favor the localization of triplet excitations on the adenine groups or AT-complexes that are the most stable.

5. CONCLUSIONS

1. While the displacements of the first excited electronic singlet and triplet levels of DNA are determined by the properties of individual nucleotides, the fluorescence and phosphorescence of DNA are due to the electronic excitation energy migration to the correspondent intramolecular traps.
2. The lowest excited electronic singlet levels of DNA are due to guanine bases, and the lowest excited triplet electronic level of DNA is connected with adenine bases.
3. Mobile triplet excitations in DNA spread at least at a distance of about 16 base pairs, and the average spreading length of singlet excitations does not exceed a few base pairs.
4. The comparative studies of DNA and its model compounds (poly $(dAdT)_2$, d(CCCGGGTTTAAA), d(ATC), d(AT), dGMP, dAMP, dCMP, and dTMP) show that the traps mentioned above for singlet excitons in the DNA macromolecule and d(CCCGGGTTTAAA) could be not only excimers (as it is pointed in [22,30]) but guanine and cytidine bases.
5. The studies of the DNA, poly$(dAdT)_2$, d(CCCGGGTTTAAA), d(ATC), and d(AT) phosphorescence, as well as the investigations on the UV-damage of DNA and poly$(dAdT)_2$, lead to the conclusion that the traps for triplet excitons in DNA, poly$(dAdT)_2$, and d(CCCGGGT TTAAA) are adenosine groups and AT-sequences that are the most photostable centers. The energy transfer to these centers leads to the manifestation of the DNA stabilization effect: the DNA self-protection against a damage caused by the appearance of electronic excitations generated by different factors (ionizing radiation, chemical reaction, UV-radiation, etc.) in the DNA macromolecule.

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