LONG-RANGE MIGRATION OF ELECTRON EXCITATION ENERGY THROUGH A DNA MOLECULE

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From the point of view of its physical properties, one giant DNA molecule constitutes a one-dimensional aperiodic molecular crystal. This is particularly pronounced in the laws governing its melting (see the reviews [1] and [2]). This one-dimensional crystal is made up of heterocyclic nitrogenous bases which are spaced 3.4 Å apart and are in close Van der Waals contact. Starting from the analogy between the construction and spectral properties of nitrogenous bases and simple cyclic hydrocarbons, we can expect common features to be observed in the optical properties of molecular crystals of benzene, naphthalene, anthracene, etc., on the one hand, and DNA on the other. In particular, a characteristic phenomenon observed in molecular crystals is the effective migration of the electronic excitation [3 - 5]. We present here experimental data evidencing that an electronic excitation migrates over large distances also through the DNA molecule.

It is known that absorption of a quantum of ultraviolet radiation produces in DNA an irreversible change in the chemical structure of individual nitrogenous bases. The main photoproducts are in this case thymine dimers [6]. They are produced by covalent bonding of two adjacent thymines and have a sandwich structure similar to that of anthracene photodimers. Their appearance leads to a local disturbance of the DNA helical structure (defect formation [2, 7]).

The sequentially disposed thymines capable of being transformed into photodimers by irradiation have a nearly random distribution over the DNA molecule. They are encountered in the T2 phage DNA, which was investigated in the present study, on the average once for every four base pairs. The probability

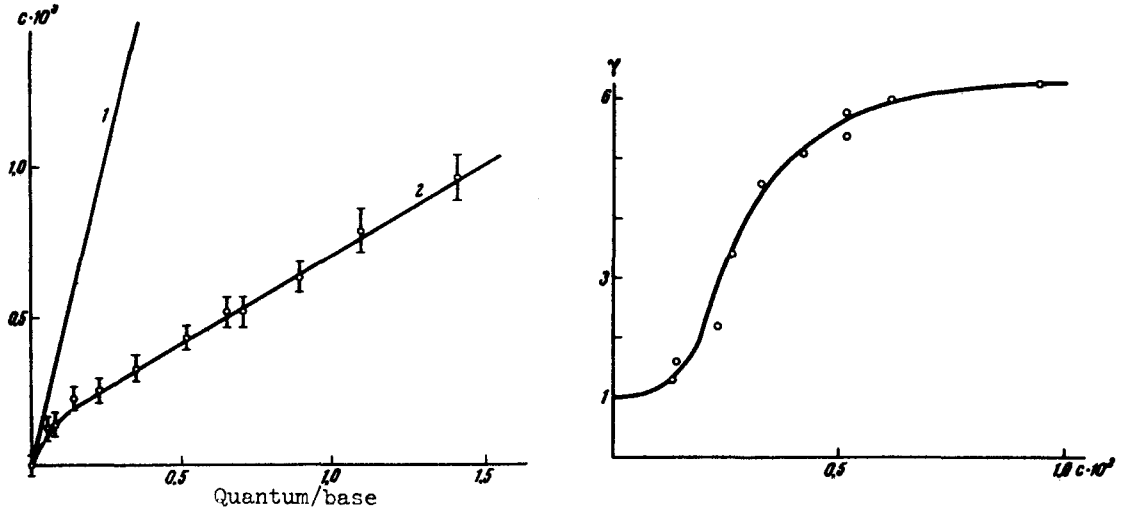

Fig. 1. Dose dependence of the concentration of thymine (curve 1), plotted in accord with our measurements and the data of [8], and of concentration of the double-helix defects (curve 2), determined by a kinetic method. We used T2 phage DNA with thymine as the tracer.

Fig. 2. Degree of bunching of thymine photodimers vs. the double-helix defect concentration.

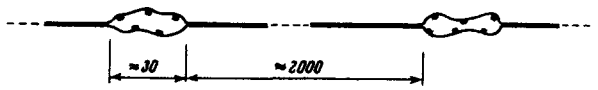

Fig. 3. Schematic representation of the structure of UV-irradiated DNA.

of absorption of a UV quantum by any base of DNA is the same and depends little on whether the base pair is untwisted or not. Therefore, if the energy of the electronic excitation is realized in the form of a photodimer only at the point of quantum absorption, then the distribution of the thymine dimers in the DNA should be close to random.

To determine the laws governing the distribution of the photodimers in irradiated DNA, we measured, by independent methods, the number of photodimers and the number of defects in the DNA double helix. The photodimers were determined by a direct method (chromatographically, cf., e.g., [6]). The number and dimensions of the defects were determined by a kinetic method [2, 7].

Figure 1 shows the dependence of the number of photodimers (curve 1) and of the number of defects (curve 2) on the UV irradiation dose. We see that the "one dimer - one defect" ratio is satisfied only at doses that are so small that approximately one dimer is obtained for 10^4 base pairs. This is particularly clearly seen in Fig. 2, which shows the dependence of the number of dimers per defect, i.e., the degree of bunching of the thymine dimers, on the defect concentration. It is also seen from Fig. 2 that even at relatively small doses, when the average distance between adjacent defects is $\sim$2000 pairs, each defect already contains on the average 5 - 6 dimers. The dimension of the defect, as shown by kinetic measurements, is only 20 - 40 base pairs. Thus, UV-irradiated DNA comprises, at the investigated doses, long undamaged helical sections alternating with short untwisted sections containing several photodimers each (see Fig. 3).

The bunching of the photodimers, i.e., the strong deviation of their distribution from random, can be explained only by assuming that the electronic excitation migrates through the DNA over long distances (on the order of 10^3 - 10^4 base pairs). The observed bunching of the thymine dimers will occur if the formation of the new dimer occurs preferentially when the migrating excitation is close to a locally untwisted section. This is natural, since the dimerization of the thymines contained in the double helix is impossible, owing to their unfavorable mutual arrangement: they are turned through an angle of 36°, whereas in the photodimers they should be located strictly one under the other. For photodimerization it is therefore essential that the thymines have a certain mobility either relative to one another, as is realized near the defect, or, with low probability, as a result of fluctuational disturbance of the helical structure, which can occur anywhere in the molecule.

The propagation of energy over large distances (on the order of one micron) is observed in crystals when the energy migrates in the form of triplet excitation (see [3, 5]). It is therefore natural to assume that in DNA the long-range energy transport is also realized via diffusion of triplet excitation. This assumption agrees well with the large lifetime of the triplet state of DNA (0.3 sec), as determined from the phosphorescence at low temperture [9]. In addition, it has been shown in a number of investigations that at low temperature the migration length of the triplet excitation exceeds, at any rate, 20 pairs [10, 11].

The standard procedure for investigating sensitized luminescence is not suitable for the observation of migration under usual conditions in the case of DNA, since DNA in solution produces hardly any luminescence. This is due, in our opinion, not to the enhancement of the vibrational relaxation, but to the high efficiency with which the photodimers are produced at room

temperature. This indeed made it possible to make use of this phenomenon for the observation of long-range excitation migration in DNA. The only circumstance that hinders the migration of the triplet excitation through the DNA is the difference between the energies of the triplet levels for different basis. This difference, however, amounts at most to 1600 cm^{-1} (0.2 eV) [6], thus reducing the probability of excitation jumps between bases by at most three orders of magnitude. Consequently, the experimentally observed diffusion displacement of the excitation (on the order of 10^4 - 10^5 Å), can occur fully within the lifetime of the triplet state in the DNA.

The notion that the photodimer is produced via a triplet excited state agrees with the results of quantum-mechanical calculations [12].

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MODEL OF FROZEN-IN (RESIDUAL) CONDUCTIVITY

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The phenomenon of frozen-in conductivity (FC), wherein the initial conductivity of cooled objects is retained for a long time after the photoexcitation is turned off [1], is presently explained on the basis of the Rose-Gibson barrier model [2 - 4]. We shall show that an analysis of the known [1 - 5] and new experimental facts leads, in an essentially unique manner, to a new FC model.

1. The experiments in which the FC was quenched with an electric field and the singularities on the quasistatic current-voltage characteristics show that noticeable effects appear in relatively weak geometric fields, $\sim 5 \times 10^3$ V/cm [1]. This circumstance, and also the nonlinearity of the dark current-ampere characteristics, offer evidence of spatial electric inhomogeneity of the semiconductor along the current lines, i.e., point to the existence of macroscopic barriers. It is natural to assume, for example, that in a polycrystalline film such barriers are due to depletion layers on the crystalline interfaces.