Charge-Transfer Excitons in DNA

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There have been a number of theoretical treatments of excitons in DNA, most neglecting both the intrachain and interchain wavefunction overlaps of the electron and hole, treating them as Frenkel excitons. Recently, the importance of the intrachain and interchain coupling has been highlighted. Experiments have shown that in $(dA)_n$ oligomers and in duplex $(dA)_n \cdot (dT)_n$, to be abbreviated (A/T), where A is adenine and T is thymine, the exciton wavefunction is delocalized over several bases. In duplexes it is possible to have charge-transfer (CT) excitons. Theoretical calculations have suggested that CT excitons in DNA may have lower energy than single chain excitons. In all the calculations of excitons in DNA, the polarization of the surrounding water has been neglected. Calculations have shown, however, that polarization of the water by an excess electron or a hole in DNA lowers its energy by $\sim 1/2$ eV, causing it to become a polaron. It is therefore to be expected that polarization charge induced in the surrounding water has a significant effect on the properties of the exciton. In what follows, we present calculations of some properties CT excitons would have in an A/T duplex taking into account the wavefunction overlaps, the effect of the surrounding water, which results in the electron and hole becoming polarons, and the ions in the water. As expected, the CT exciton has lowest energy when the electron and hole polarons are directly opposite each other. By appropriate choice of the dielectric constant, we can obtain a CT exciton delocalized over the number of sites found in photoinduced absorption experiments. The absorption threshold that we then calculate for CT exciton creation in A/T is in reasonable agreement with the lowest singlet absorption deduced from available data.

1. Introduction

The nature of the excitations created when DNA is excited by photon frequencies at the absorption edge and beyond has been debated almost since the time of discovery of DNA.[1] The general expectation was that excitons would be created. Although the finding of fluorescence from a single excited base in water[2] indicated that an exciton could occupy a single base, there was considerable debate as to whether in a multi-base DNA the exciton would be delocalized over a number of bases. It was argued early on that the fact that the UV absorption spectra of extended chain DNA closely resemble the sum of the absorption spectra of the constituent bases shows that the exciton is always localized on a single base.[1,3] However, it was shown recently that this argument is invalid; interaction of the monomers causes only slight shifts of the absorption spectra.[4] It was also found in early work that the excitation produced by photon absorption could spread over two stacked bases as an excimer (if the two bases are the same) or an exciplex (if they are different).[1,5,6] Examples are A−A and A−T. The excimers and exciplexes were discovered by the fact that they are fluorescent, the emission being red-shifted from that of corresponding dilute monomer mixtures.

Over the years, there have been many studies of photon absorption by DNA. It has been established that a singlet A monomer in solution in the form of AMP (adenosine-5-monophosphate) decays within 0.33 ± 0.3 ps by internal conversion.[7] The absolute radiative probability of AMP has been measured as 0.7×10^{-4}.[8] It is now generally agreed that on exposure to UV most excitations in stacked DNA decay to long-lived, ~ 100 ps, non-emissive states. Recent efforts to characterize these states in all A monomers and A/T duplexes led one group to declare them excimers[7] and another to characterize them as delocalized excitons.[9]

The first group, making absorption measurements on $(dA)_{18}$ at 570 nm, found a rapid initial decay with time constant $\tau = 0.8 \pm 0.16$ ps that they attribute to isolated adenine singlets because of the similarity to the AMP decay. This was followed by a much slower relaxation with time constant $\tau_2 = 126 \pm 8$ ps.[7] They assigned the latter to singlet excimers. No proof was given, however, that the excitations are excimers. It was stated that the decay time for $(dA)_{18} \cdot (dT)_{18}$ is close to that for $(dA)_{18}$, but quite different from that for $(dAdT)_9 \cdot (dAdT)_9$. Apparently on this basis they state that "intrastrand excimer states with lifetimes of $50-150$ ps are formed in high yields whenever A is stacked with itself or T," limiting "excitation energy to one strand at a time in the B-form double helix, enabling repair using the undamaged strand as a template." From their 570 nm absorption data, Crespo-Hernandez et al. estimate the yield of excimers as $\sim 65\%$. They note that the 65% figure, compared with the 79% of stacked bases expected in poly(dA),[10] would indicate that nearly every excitation decays to a non-emissive excimer. Their conclusions have been questioned by Markovitsi et al.[11−13] In the latter references it is pointed out that, if (dA) excimers were the dominant species created during excited-state relaxation in poly(dA).poly(dT), its steady-state fluorescence spectrum should be similar to that of poly(dA) because the fluorescence quantum yield of poly(dA) is much larger than that of poly(dT). However, the data of ref 12 show that not to be the case.

Buchvarov et al. studied photoinduced absorption (PA) of $(dA)_n$ and $(dA)_n \cdot (dT)_n$ over a wide range of frequencies ($300-700$ nm) after pumping at 270 nm. They were in agreement

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with the results of ref 7 in finding two different excited-state processes, one with a lifetime of hundreds of femtoseconds, attributed to poorly stacked single bases, another with a lifetime of about a hundred picoseconds.[9] Also in agreement with ref 7, they attributed the latter process to stacked regions. However, they differ from ref 7 in assigning the latter processes to delocalized excitons rather than to excimers.

Studying the PA as a function of frequency, they found that the short wavelength (<380 nm) behavior for $(dA)_n$ and duplexes $(dA)_n \cdot (dT)_n$, $n > 1$, was similar to that of AMP; they therefore interpreted the PA in that region as due to localized bases.[9] To determine the origin of the long-wavelength (>420 nm) behavior they studied how the intensity ρ_{435} of the PA observed in a narrow wavelength region around 435 nm (normalized to the PA due to the localized transition at 330 nm) varied with the number of bases n of $(dA)_n$. They found, from data taken 3 ps after excitation, a dependence of ρ_{435} on n up to about 8 bases. From this they determined the "1/e delocalization length" for $(dA)_n$ as 3.3 ± 0.5 bp or 11.2 ± 1.7 Å.[9] Although they have fewer data for duplexes $(dA)_n \cdot (dT)_n$, they surmised that the "1/e delocalization length" for that case is similar, although slightly larger. Another finding was that plots of ρ_{435} versus time show a decrease with time by about 1/3 of their initial value before coming to a steady value, the rate of decrease corresponding to a relaxation time $\tau = 8 \pm 1$ ps for both $(dA)_n$ and duplexes $(dA)_n \cdot (dT)_n$.[9]

Clearly there is incompatibility between the results of Crespo-Hernandez et al. on the one hand and those of Buchvarov et al. and Markovitsi et al. on the other. With evidence for a characteristic length of an exciton over 3As in $(dA)_n$, the Buchvarov et al. results rule out excimers being the predominant excitation for chains over 3As in length. They do not rule out, however, excimers being the predominant excitation for chains 2A and 3A in length. In this connection, we note that a recent theoretical study of the excited-state properties of a stacked dimer of 9-methyladenine in B-DNA conformation, immersed in aqueous solution, has, according to the authors, provided strong evidence in support of a fast transfer from the bright spectroscopic state to an excimer-like state.[14] In this paper, we limit our discussion to DNAs that are three or more bases in length.

Theoretical work on excitons in DNA started with Rhodes[15] and Tinoco[16] in 1959 and 1960. In this work the singlet excitons were treated as separate chromophores or Frenkel excitons, as subsequently set out by Rashba[17] and Davydov[18] in the so-called exciton model. The model is applicable to a series of weakly coupled monomeric chromophores. In this model, the excited states of the chromophores are taken to be linear combinations of the excited states of each monomeric chromophore. The exciton properties are obtained by diagonalization of the Hamiltonian matrix, in which the diagonal terms represent the excitation energies of the monomer transitions and the off-diagonal term represents the electron coupling of the dipoles. In recent work, focusing on all A or A/T DNA, introduction of quantum chemistry methods has improved the accuracy of the calculations.[18,20,4] In a perfectly periodic arrangement of the chromophores, the model leads to a Frenkel exciton that is extended over the length of the DNA. To achieve an exciton of finite length it is necessary to introduce disorder.[20] There are serious shortcomings in this model, specifically: (1) neglect of the intra- and interchain coupling due to wavefunction overlap of the chromophores, the DNA bases; and (2) neglect of the polarization of the solution surrounding the DNA. In refs 4 and 20, water was included in the calculations, but it played only

the minor role of being involved in the conformation of the double helix. For a single charge, an excess electron, or a hole, the polarization of the water limits the size of the wavefunction to several sites,[20,22] how many depending on the sequence,[23] and turns the charge into a polaron, which must drag the polarization with it as it moves.[21,24,25] It has been shown that viewing the charge as a polaron can explain many experimental observations.[21,25−27] An exciton, consisting of two opposite charges, will undoubtedly give rise to less net polarization of the surrounding water and ions than a polaron, but polarization will still affect its properties.

A quite different theoretical study of excitons in DNA has been carried out recently by Starikov et al.[28] They analyzed the electronic structure of stacked base pair dimers using ab initio Hartree−Fock and semiempirical Hartree−Fock configuration interaction quantum chemistry. These studies include the base pair A/T stacked on A/T, as well as many other dimeric sequences. Although the calculations were done for DNA in vacuum and the limitation to base pair dimers means that the excitons are somewhat shorter that those found experimentally in ref 9, some of the qualitative conclusions of this study should be meaningful for the actual situation in DNA. Starikov et al. state that their most important finding is that the first excited states of DNA duplexes are predominantly of CT exciton parentage, and not a product of mixing between Frenkel exciton and CT exciton states[28] as in the conventional organic molecular solids, and as has been assumed in applying the molecular exciton model to DNA. As support for this finding, they point out that the actual ionization potentials (IPs) of the DNA bases are much lower than the values found for isolated bases in a vacuum, ∼6 to 8 eV, and close to the lowest optical excitation energies, ∼4 to 5 eV.[29−33] The lowering of the IPs is attributed to the inter- and intra-band (base stacking) base coupling and interaction between the bases and their environment of water and ions.[21] The origin of the CT exciton in DNA is attributed to hydrogen bonding between purines and pyrimidines within the base pairs, owing to which the HOMO resides on the purine residue and the LUMO on the pyrimidine residue.[28]

Although there is no direct experimental evidence for CT excitons of the type we are discussing, Markovitsi et al. have shown that decay times of poly(dA).poly(dT) vary considerably, so that at 330 nm, for example, 20% of the photons are emitted at times larger than 100 ps. They suggest that this long time behavior may be due to states built with participation of charge-transfer interactions.[12,13]

2. The Model and Calculations

The calculations to be described were carried out for an A/T duplex with B geometry assumed. As we have done previously,[21,24−26] we modeled the DNA as a series of bases placed inside a cylindrical cavity having the radius R of the double helix. Water and ions are outside the cavity but none inside due to the hydrophobicity of the bases. In this paper, as in ref 25, the bases are taken to be on two straight chains at distances $+R_h$ and $-R_h$, respectively, from the axis of the cylinder; it was shown that neglecting the helical structure of the base stack does not lead to significant error.[27] We assume that the hole is delocalized over the chain of As and the electron over the chain of Ts.[34] The presence of water results in localizing them on their respective chains, creating a hole polaron coupled to an electron polaron, our charge-transfer exciton.

We suggest that evidence for our model, in particular the effect of water, is the finding of ref 9 mentioned earlier, that plots of ρ_{435} versus time show a decrease of ∼1/3 with time,

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TABLE 1: Values of $g^{jj'}_{n-n'}$

$n-n'$	g^{11} and g^{22} (eV)	g^{12} and g^{21} (eV)
1	−1.367	−1.157
2	−1.322	−1.130
3	−1.201	−1.053
4	−1.054	−0.951
5	−0.910	−0.843
6	−0.781	−0.738
7	−0.677	−0.649
8	−0.593	−0.574
9	−0.523	−0.510

corresponding to a relaxation time $\tau = 8 \pm 1$ ps for both (dA)$_n$ and duplexes dA/dT. We note that 8.3 ps is the orientational relaxation time at 298 K for the dielectric screening by water molecules.[35,21] Orientation of the water dipoles around the DNA, whether single-strand or duplex, can be expected to stabilize the excitons, as it does polarons in DNA,[21,25,27] and thus reduce the transitions giving rise to PA at 435 nm and other frequencies in the long-wavelength range.

The Hamiltonian may be written as the sum of three terms. The first, H_0, is the one-dimensional tight binding Hamiltonian

$$H_0(\psi_{n,j}\psi^*_{n,j}) = -\Sigma_{n,j}\, t_{n,j;\,n+1,j}\psi_{n,j}\psi^*_{n+1,j} \quad (1a)$$

where $\psi_{n,j}$ is the amplitude of the wavefunction of the hole or excess electron at the nth base in the jth chain ($j = 1,2$) and $-t_{n,j;\,n+1,j}$ is the transfer integral for the hole or excess electron. The resulting matrix elements may be writtenas follows:

$$H_{n,n\pm1}^{A} = -t_0^{A} \quad (1b)$$

$$H_{n,n\pm1}^{T} = -t_0^{T} \quad (1c)$$

for the A chain and T chain, respectively, and $-t_0^A$, $-t_0^T$ are the transfer integrals for two adjacent As and two adjacent Ts, respectively.

The second term of the Hamiltonian, taken from ref 27,

$$H_{w} = (1/2)\, \Sigma_{n,n'}\Sigma_{j,j'}g^{jj'}_{n-n'}|\psi_{n,j}|^2|\psi_{n',j'}|^2 \quad (2)$$

represents the effect on the hole or excess electron energy of the polarization charge it induces in the surrounding water. The summations over n and n' are to be taken over all the sites on a chain. The coefficients $g^{jj'}_{n-n'}$ depend only on R and R_h; they were evaluated by the solution of the electrostatic problem in ref 27. Their values are shown in Table 1.

Calculations of the eigenvalues were simplified by including the $g^{jj'}_{n-n'}$ terms in the diagonal matrix elements. Thus, with the Ts taken as chain 2, the diagonal matrix element for the electron becomes

$$H_{n,n} = (1/2)\, \Sigma_{n'}(-|g^{22}_{n-n'}| + |g^{21}_{n-n'}|)\, |\psi_{n',2}|^2 \quad (3)$$

The term $g^{22}_{n-n'}$ represents the effect on the electron energy of the positive polarization charge induced by the electron, while $g^{21}_{n-n'}$ represents the effect on the electron energy of the negative polarization charge induced by the A-chain hole. On the adenine chain, chain 1, a similar expression holds for the matrix elements with $g^{22}_{n-n'}$ replaced by $g^{11}_{n-n'}$, $g^{21}_{n-n'}$ replaced by $g^{12}_{n-n'}$, and the signs changed appropriately. As has been shown,[25] $|g^{11}_{n-n'}| = |g^{22}_{n-n'}|$ and $|g^{12}_{n-n'}| = |g^{21}_{n-n'}|$.

The third term of the Hamiltonian represents the Coulomb interaction between the hole and the excess electron. Written for an anisotropic dielectric medium with dielectric constants

$\epsilon_\parallel$ and $\epsilon_\perp$ parallel and perpendicular to the chain direction, respectively,[36] the matrix element for the electron corresponding to this term is

$$H_{n,n} = -e^2 \Sigma_{n'}|\psi_{n',1}|^2/\epsilon_\perp[(n-n')^2a^2 + (\epsilon_\parallel/\epsilon_\perp)(2R_h)^2]^{1/2} \quad (4)$$

where a is the distance between neighboring bases, 3.4 Å for B-DNA, and the sum is taken over the adenine sites. For the hole diagonal matrix element the sum is taken over the thymine sites and the sign in front is + because a decrease in energy of a hole moves it to a higher electronic level.

Unfortunately, $\epsilon_\parallel$ and $\epsilon_\perp$ are not known. With water excluded from the interior of the DNA and no other free charges in the cavity, one might guess that $\epsilon_\parallel$ and $\epsilon_\perp$ are unity, making the magnitude of the Coulomb energy of the electron and hole greater than 2 eV! Considerable research has been done on dielectric constants for the interior of proteins. It has been found that the effective dielectric constant for the interaction of two separated ionized charges in the interior of a protein is quite large, >15.[37] Commenting on this, King et al. say "Apparently the protein sites near ionized groups are very polar."[37] We expect that DNA would show similar behavior, although the effective dielectric constant should be smaller because of the simpler structure of DNA. Since calculation of the effective dielectric constant is difficult and complicated,[37] we took $\epsilon_\perp = 1$ and $\epsilon_\parallel$ as the value required to give the length of the CT exciton in agreement with the exciton length found in ref 9.

With separate Hamiltonians for the electron and hole it is necessary to ensure self-consistency of the solutions. To do this we diagonalized the electron Hamiltonian first with an assumed set $\psi_{n',j'}$ for the hole wavefunction. This leads to a set of $\psi_{n,j}$ for the electron wavefunction which we then use to diagonalize the hole Hamiltonian, obtaining a new set of $\psi_{n',j'}$. The electron Hamiltonian is diagonalized again with this new set. The procedure is repeated until it converges to a pair of consistent solutions for the two chains.

3. Choice of Parameters

The quantity t_0^A has been calculated as 0.03 eV for holes by several groups.[38−40] Calculations of transfer integrals for electrons are rarer. For an electron on adjacent Ts, a preliminary estimate of t_0^T was given as 0.02 eV.[41a,b] As noted earlier, dependence of the polaron energy on the transfer integral is not strong.[21] The parameter R_h was, as noted above, chosen as 0.3 nm, this being fairly closely the distance between the center of each of the four bases and the axis of the helix. R was taken as the radius of the helix, 1 nm.

As discussed above, we have chosen the value of $\epsilon_\parallel$ as the value required to make our calculated length for the charge-transfer exciton agree with the length found by Buchvarov et al. for the excitations in the case of the duplex. They found the "1/e exciton delocalization length" for the sequence (dA)$_n$ to be 3.33 ± 0.5 base pairs. Of course this exciton is not a charge-transfer exciton because (dA)$_n$ is single-stranded. However, their investigations on A/T duplexes led to a similar length, although perhaps a little larger, for the entity that they call an exciton in that case, which could in principle be a charge-transfer exciton. The value of $\epsilon_\parallel$ that yields a length for our charge-transfer exciton of about 4 base pairs is 4.

4. Results and Discussion

The result of our calculations for the CT exciton with the hole on A, electron on T, and the parameters we have assumed, is that for minimum energy the hole and electron are directly
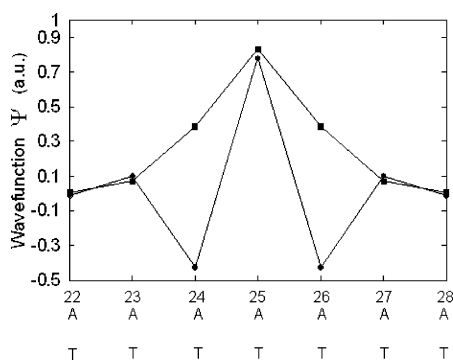
Figure 1. Calculated wavefunction of charge-transfer exciton vs base position: hole ● on A chain of A/T duplex; electron ■ on T chain of A/T duplex.
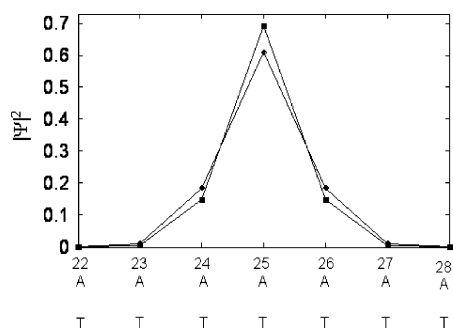

Figure 2. Calculated $|\Psi|^2$ of charge-transfer exciton vs base position: hole ● on A chain of A/T duplex; electron ■ on T chain of A/T duplex.

opposite each other, as shown in Figures 1 and 2, with the hole energy level shifted 0.725 eV above the adenine HOMO and the electron energy level shifted 0.709 eV below the thymine LUMO. The displacements of the energy levels are expected to be close to each other in size because, as calculated here, the only difference between the hole and electron properties is that $t_0^A \neq t_0^T$. This difference affects the part of the energy shift due to water polarization but, as will be seen, the effect is quite small.

Because the polarization charges due to the hole and electron have opposite signs, their effects tend to cancel, as is shown explicitly in eq 3. The cancellation should be considerable because $g^{12}_{n-n'}$ is close in magnitude to $g^{11}_{n-n'}$ (see Table 1). Thus the largest term in the Hamiltonian, eqs 1–4, is expected to be the one due to the Coulomb attraction of the electron and hole polarons. As noted above, if the electron and hole wavefunctions were each concentrated on a single site, the sites being opposite to one another, and both ϵ's were unity, the Coulomb term deduced from eq 4 would be <−2 eV. For $\epsilon_\perp =$ 1 and $\epsilon_\parallel$ chosen as 4 to result in a CT exciton spreading over ∼4 base pairs, as seen in Figures 1 and 2, the Coulomb attraction would be ∼0.6 eV. Thus, as anticipated, the Coulomb term is dominant over the water polarization terms.

According to our calculations, creation of the CT exciton envisioned here requires raising an electron from the HOMO level of A to the level 0.709 eV below the LUMO level of T. With the energy difference between the LUMO of T and the HOMO of A denoted by the quantity Δ, the energy required to create a CT exciton may be taken as $\Delta = 0.7$ eV. If we assume the transition is so rapid that the water polarization has not yet taken place, the energy required would be $\Delta = 0.6$ eV. Δ is not, of course, known accurately for this situation but it should be, within a few tenths of an electronvolt, equal to the IP of A in aqueous solution. Measurements of Marguet et al. on duplexes containing adenines and thymines showed one-photon ionization

occurring at 4.66 eV. Taking Δ as 4.6 eV we find the threshold for CT exciton creation is 4 eV within a few tenths of an electronvolt. Unfortunately, there are no data available for the optical absorption threshold of an A/T duplex. Data for $(dA)_{18}$-$(dT)_{18}$ show that its absorption close to the absorption edge is quite similar to that of AMP.[9] It is reasonable to conclude that the absorption edge for A/T is close to that of AMP. This would result in our calculated absorption edge for the CT exciton being in reasonably good agreement with what we presume to be the edge.

We note that the energy of the CT exciton need not be higher than that of what we could call a single-chain exciton, that is, an exciton where the electron and hole wavefunctions are both mainly on the same chain, with the electron having been raised considerably in energy. If the electron and the hole were on the same strand, although of course separated from each other, the effects of the water polarization would to a good extent cancel, probably more so than in the CT exciton. Probably the cancellation is more exact for the single-chain exciton. Also the Coulomb attraction term is likely to be smaller than for the CT exciton. As noted earlier, the 1/e localization length of the single-chain exciton found in ref 9 is 11.7 Å. Thus the electron and hole in the single-chain exciton are likely to be more than 0.6 nm apart, whereas 0.6 nm is the separation of the electron and hole in the CT exciton when they are opposite each other.

The electron and hole polarons in the CT exciton need not be stationary but can move along their respective strands. Moving away from the position opposite each other decreases their Coulomb energy, changing their energy levels. Although this motion might increase the energy due to water polarization by decreasing the cancellation of the opposing charges due to the two chains, that effect is expected to be much smaller than the decrease in the Coulomb energy. Another type of motion that could have a strong effect on the CT exciton energy is that in response to a phonon whose vibrations have a component transverse to the chains, thus modulating the Coulomb attraction of the electron and hole. It has been shown that interaction with such phonons results in the optical absorption spectrum taking the form of broad Gaussian curves.[44] This could account for some of the observed long spectral tail of the PA to low frequencies observed in ref 9.

Fluctuations could also have a big effect, particularly in view of the vibrationally hot ground states resulting from the decay through internal conversion of the excited singlets.[45] Studies of the effects of environmental fluctuations have been carried out by several groups. In one study it was found that room-temperature fluctuations cause the relative energy of an adjacent adenine and guanine to vary from a high of 1.2 eV to a low of −0.3 eV in a 12 ns time interval.[46] It has also been shown that structural fluctuations have strong effects on electronic coupling of adjacent bases.[47,48] Through all these effects, fluctuations could result in transitions between exciton levels and in exciton hopping, both of which could contribute to the long tail observed in the photoinduced absorption. It might be considered that CT exciton hopping would be less probable than hopping on chain by a single chain exciton but, as pointed out earlier, in a duplex the exciton wavefunction is in any case spread over both chains.

In conclusion, we have calculated the properties of a CT exciton in dA/dT taking into account the effect of the surrounding water and intra- and interchain interactions. We find it to be delocalized over several sites, which would be in agreement with the experimental findings of Buchvarov et al., and have an absorption threshold comparable to that found for singlets in dA/dT DNA. Although there is no direct experimental

evidence for such excitons, on the basis of their measurements of long-time transient absorption in $(dA)_{18}\cdot(dT)_{18}$, Markovitsi et al. have suggested that the species observed in those measurements could well be interstrand A−T charge-transfer states.[11] To establish whether CT excitons can be created in DNA, as suggested by Starikov et al., one could carry out electro-absorption or nonlinear optical experiments. It would also be useful to obtain more data of the kind found in ref 9 on duplexes, to investigate in particular whether the exciton is localized over more sites in longer duplexes.

References and Notes

(1) For a general discussion of early progress in this field, see Guéron, M.; Eisinger, J.; Lamola, A. A. Excited states of nucleic acids. In *Basic Principles in Nucleic Acid Chemistry*; Ts'o, P. O. P., Ed.; Academic Press: New York, 1974; Vol. 1, pp 311−398.

(2) Guéron, M.; Eisinger, J.; Shulman, R. G. *J. Chem. Phys.* **1967**, *47*, 4077−4091.

(3) Eisinger, J.; Shulman, R. G. *Science* **1961**, *161*, 1311−1319.

(4) Emanuele, E.; Markovitsi, D.; Millié, P.; Zakrzewski, K. *Chem. Phys. Chem.* **2005**, *6*, 1387−1392.

(5) Eisinger, J.; Guéron, M.; Shulman, R. G.; Yamane, T. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *55*, 1015−1020.

(6) Vigny, P. *C. R. Acad. Sci. D* **1973**, *277*, 1941−1944.

(7) Crespo-Hernandez, C. E.; Cohen, B.; Kohler, B. *Nature* **2005**, *436*, 1141−1144.

(8) Crespo-Hernandez, C. E.; Kohler, B. *J. Phys. Chem. B* **2004**, *108*, 11182−11188.

(9) Buchvarov, I.; Wang, Q.; Raytchev, M.; Trifonov, A.; Fiebig, T. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 4794−4797.

(10) Dewey, T. G.; Turner, D. H. *Biochemistry* **1979**, *18*, 5757−5762.

(11) Markovitsi, D.; Talbot, F.; Gustavsson, T.; Onidas, D.; Lazarotto, E.; Marguet, S. *Nature* **2006**, *441*, E7.

(12) Markovitsi, D.; Onidas, D.; Gustavsson, T.; Talbot, F.; Lazarotto, E. *J. Am. Chem. Soc.* **2005**, *127*, 17130−17131.

(13) Markovitsi, D.; Gustavsson, T.; Talbot, F. *Photochem.Photobiol. Sci.* **2007**, *7*, 717−724.

(14) Santoro, F.; Barone, V.; Improta, R. *Proc. Natl. Acad. Sci U.S.A.* **2007**, *104*, 9931−9936.

(15) Rhodes, W. *J. Am. Chem. Soc.* **1961**, *83*, 3609−3617.

(16) Tinoco, I. *J. Am. Chem. Soc.* **1960**, *82*, 4785−4791.

(17) Rashba, E. I.; Sturge, M. D. *Excitons*; North-Holland: Amsterdam,

(18) Davydov, A. S. *Theory of Molecular Excitons*; McGraw-Hill: New York, 1962.

(19) Bouvier, B.; Gustavsson, T.; Markovitsi, D.; Millié, P. *Chem. Phys.* **2002**, *275*, 75−92.

(20) Bouvier, B.; Dognon, J.-P.; Lavery, R.; Markovitsi, D.; Milié, P.; Onidas, D.; Zakrzewski, K. *J. Phys. Chem. B* **2003**, *107*, 13512−13522.

(21) Basko, D. M.; Conwell, E. M. *Phys. Rev. Lett.* **2002**, *88*, 098102.

(22) Kurnikov, I. V.; Tong, G. S. M.; Madrid, M.; Beratan, D. N. *J. Phys. Chem. B* **2002**, *106*, 7−10.

(23) Conwell, E. M.; Bloch, S. M. *J. Phys. Chem. B* **2006**, *110*, 5801−5806.

(24) Conwell, E. M.; Basko, D. M. *J. Phys. Chem. B* **2006**, *110*, 23603−23606.

(25) Conwell, E. M. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8795−8799.

(26) Park, J.-H.; Choi, H.-Y.; Conwell, E. M. *J. Phys. Chem. B* **2004**, *108*, 19483−19486.

(27) Conwell, E. M.; Bloch, S. M.; McLaughlin, P. M.; Basko, D. M. *J. Am. Chem. Soc.* **2007**, *129*, 9175−9181.

(28) Starikov, E. B.; Lewis, J. P.; Sankey, O. F. *Int. J. Mod. Phys. B* **2005**, *19*, 4331−4357.

(29) Sugiyama, H.; Saito, I. *J. Am. Chem. Soc.* **1996**, *118*, 7063−7068.

(30) Kawai, K.; Wata, Y.; Ichimose, N.; Majima, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4327−4329.

(31) Kim, N. S.; Zhu, Q.; LeBreton, P. R. *J. Am. Chem. Soc.* **1999**, *121*, 11516−11530.

(32) Zhu, Q.; LeBreton, P. R. *J. Am. Chem. Soc.* **2001**, *122*, 12824−12834.

(33) Papadantonakis, G. H.; Tranter, R.; Brezimsky, K.; Yang, Y.; VanBreomen, R. B.: LeBreton, P. R. *J. Phys. Chem. B* **2003**, *106*, 7704−7712.

(34) Note that, apart from the homoadenines, it is not to be expected that either the electron or hole wavefunction is confined to a single chain. As we showed in our calculations for a hole on an A/T duplex (ref 25), a small part of the hole wavefunction was on the T chain. Similarly, for the CT exciton a small part of the hole wavefunction is expected to be on the T chain and a small part of the electron wavefunction on the A chain. This division of the wavefunction did not have much effect on the properties of the hole polaron, and we assume there is a similar lack of effect for the CT polaron.

(35) Kaatze, V. *J. Chem. Eng. Data* **1989**, *34*, 371−374.

(36) Landau, L.; Lifshitz, E. M. *Electrodynamics of Continuous Media*; Pergamon Press: Oxford, 1960; pp 61−62.

(37) King, G.; Lee, K. S.; Warshel, A. *J. Chem. Phys.* **1991**, *95*, 4366−4376.

(38) Voityuk, A. A.; Rösch, N.; Bixon, M.; Jortner, J. *J. Phys. Chem. B* **2000**, *104*, 9740−9745.

(39) Grozema, F. C.; Siebbeles, L. D. A.; Berlin, X. A.; Ratner, M. A. *Chem. Phys. Chem.* **2002**, *2*, 536−539.

(40) Senthilkumar, K.; Grozema, F. C.; Fonseca Guerra, C.; Bickelhaupt, F. M.; Lewis, F. D.; Berlin, Yu. A.; Ratner, M. A.; Siebbeles, L. D. A. *J. Am. Chem. Soc.* **2005**, *127*, 14894−14903.

(41) (a) Voityuk, A. A.; Michel-Beyerle, M.-E.; Rösch, N. *Chem. Phys. Lett.* **2001**, *342*, 231−238. (b) Voityuk, A. A. *J. Chem. Phys.* **2005**, *123*, 034903.

(42) Li, X.; Cai, Z.; Sevilla, D. *J. Phys. Chem. A* **2002**, *106*, 1596−1603.

(43) Marguet, S.; Markovitsi, D.; Talbot, F. *J. Phys. Chem. B* **2006**, *110*, 11037−11039.

(44) Agranovich, V. M.; Zakhidov, A. A. *Chem. Phys. Lett.* **1977**, *50*, 278−281.

(45) Pecourt, J.-M. L.; Peon, J.; Kohler, B. *J. Am. Chem. Soc.* **2001**, *123*, 10370−10378.

(46) Voityuk, A. A.; Siriwong, K.; Rösch, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 624−627.

(47) Voityuk, A. A.; Siriwong, K.; Rösch, N. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5421−5425.

(48) Troisi, A.; Orlandi, G. *J. Phys. Chem. B* **2002**, *106*, 2093−2101.