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DNA Conformations

Towards an Understanding of Stacked Base Interactions: Non-Equilibrium Phase Transitions as a Probable Model

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Summary

The distances of stacked bases of DNA in different conformations cannot be calculated by equilibrium potentials, since they exhibit not more than only one minimum. However, a double potential minimum is obtained by considering the most simple semiclassical model of excitons that are coupled adiabatically to lattice vibrations, hence forming polaritons. By use of Danilov's extended Hückel approximation of DNA excitons, stacked base distances can be calculated that agree fairly well with the experimental data. The errors of this approach are small as compared to the differences of the distances in various conformations. Consequently, this model may work as a first base of understanding molecular interactions in DNA.

Introduction

It is well known that the stationary state distances of stacked bases of DNA display potential minima of the corresponding interaction energy. The large difference of the experimental values of the vertical base pair distances in different DNA conformations, for instance 2.6 Å of the A-form and 3.4 Å in the B-form (1-4), cannot be explained in terms of the usual dipole-dipole, dipole-induced dipole and dispersion interactions energies of purine and pyrimidine ground states. This follows from extented calculations of DNA-interactions energies (for instance (5)), which can never result in a double potential minimum of vertical interactions between stacked bases. Consequently, non-equilibrium phenomena have to be considered, in order to understand the stationary state distances of stacked bases of DNA in different conformations. This consequence, which is in line with Prigogine's theory of dissipative structures, is not entirely new (6,7) and holds even in quasi-equilibrium situations, if the life time of excited states is considerably long.

Phase transitions of solitons, that have been claimed for understanding the dynamics of DNA conformations (8) and hence also its geometry are, of course, a possible source of influence on the distances of stacked bases in different conformations, too. There arise, however, at the one hand, difficulties in understanding the rather stationary state distances of DNA with this model. External influences (cations, water, hydration), on the other hand, cannot explain the large difference in base distances (about 2.6 A and 3.4 Å, respectively) between the A and B form of DNA.

We suggested, for several reasons that exciplex formation is a fundamental non-equilibrium process in DNA (9). This exciplex model does not exclude several potential minima, because the molecular couplings are assumed to be very strongly localized. Moreover, it allows distinct interaction potentials which are rather stable against external influences. It appears, therefore, reasonable, to calculate the potential minima of the known ex-

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ciplex potential of DNA base pairs (10) and to compare them with the experimental data.

Results and Discussion

According to a semiclassical adiabatic approach, spatial and temporal parts of the DNA interactions can be factorized. This most simple model delivers the potential for a stationary state, and allows to decide whether more detailed calculations may be useful or not.

Denoting the interaction potentials of the exciplex state and its ground state, $V_1(x)$ and $V_2(x)$, respectively, where x represents the vertical distance of stacked base pairs, the average potential $V(x,t)$ is given by

$$V(x,t) = \frac{N_1(t)}{N} \cdot V_1(x) + \frac{N_2(t)}{N} \cdot V_2(x) \qquad (1)$$

$N_1(t)$ and $N_2(t)$ are the numbers of electrons occupying the levels $V_1(x)$ and $V_2(x)$ at time t, respectively. N is the average number of electrons within the exciplex system. As long as N remains constant, the system can remain in the stationary state. The sufficient condition of stationarity is then obtained from the rate equations of an exciplex system (11):

$$\dot{N}_1 + \tfrac{1}{2}\dot{N}_2 = 0 \qquad (2)$$

The factor $\frac{1}{2}$ reflects the fact that one excited state is obtained for each two bases in the ground state. This fact may be important for the doubling capacity of this macromolecule.

The potential equ. (1) gives rise to vertical oscillations of the base pairs around two stationary state positions X_1 and X_2. Actually, we obtain by optimization $dV = 0$, and keeping N constant

$$(\dot{N}_1 V_1 + \dot{N}_2 V_2)\, dt + (N_1 V_1' + N_2 V_2')\, dx = 0$$

resulting in

$$\frac{dx}{dt} = \dot{x} = -\frac{\dot{N}_1 V_1 + \dot{N}_2 V_2}{N_1 V_1' + N_2 V_2'} \qquad (3)$$

A stable distance is only achieved for $\langle\dot{x}\rangle = 0$, where $\langle\ldots\rangle$ denotes the time average over one period of oscillation. This means that solutions of equ. (3) have to be found, where either the nominator vanishes or, in case of a vanishing denominator, the nominator vanishes in such a way that equ. (3) provides a vanishing $\langle\dot{x}\rangle$ too.

The first possible solution of $\langle\dot{x}\rangle = 0$ is obtained, when we substitute equ. (2) into equ. (3) for $\dot{x} = 0$. Then holds

$$V_1(X_1) = 2V_2(X_1) \qquad (4a)$$

For the second possible solution, $\dot{x}$ has obviously to change its sign for a given set of N_1 and N_2. By use of the well-known rule of l'Hospital it can be easily shown that in this case equ. (3) vanishes, if and only if

$$\langle\dot{N}_1\rangle = \langle\dot{N}_2\rangle = 0 \quad \text{with } N_1 = N_2$$

and

$$V_1'(X_2) = -V_2'(X_2) \qquad (4b)$$

For our purpose it suffices to use approximations of the potentials $V_1(x)$ and $V_2(x)$ for AA-, GG-, UU-, and CC-excimers. TT-excimers would shift X_1 and X_2 to slightly higher values. Taking into account the calculated potentials of Danilov et al. (10) which, on the basis of MO-theory, deliver the so far most accurate results, we can then scribe approximately

$$V_1(x) = 4.5 \exp\left(-\frac{5}{3}(x-x_o)\right) + 8.25 \ln\left(\frac{x}{x_o}\right) \quad (5a)$$

$$V_2(x) = 4.5 \exp\left(-\frac{11}{3}(x-x_o)\right) \quad (5b)$$

V is taken in units of eV, x in Å. For x_o = 2.4 Å, V_1 and V_2 become equal.

The formulae (3) are with sufficiently high accuracy valid in the region 2.4 Å < x < 3.8 Å. The coefficients have been adjusted to the minimum of V_1, and the boundary values of V_1 and V_2 according to ref. (10).

By use of (4a) we get

$$X_1 = 2.6 \pm 0.1 \text{ Å} \quad (6a)$$

Differentiation of equ.(5) and insertion into equ.(4) result finally in

$$X_2 = 3.3 \pm 0.2 \text{ Å} \quad (6b)$$

The uncertainties in the approximation of Danilov's calculations have there been considered.

X_1 agrees well with the known vertical distance of base pairs in the A-form (2.6 Å), while X_2 reflects the experimental data of the other DNA conformations (3.0 to 3.8 Å), if considering the sensitive dependence of X_2 on the denominator of the term on the RHS of equ.(3). In particular, a rather strong influence of this distance on external forces can be expected. The error of these calculated stationary state distances is, however, small compared to the actual differences of 0.6 Å of these distances themselves such that the model is strongly supported by the actual quantitative results.

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