Static first order hyperpolarizabilities of DNA base pairs:
A configuration interaction study

Prasenjit Seal [a], Prakash Chandra Jha [b,1], Swapan Chakrabarti [a,*]

[a] *Department of Chemistry, University of Calcutta, 92 A.P.C. Ray Road, Kolkata 700 009, India*
[b] *Department of Theoretical Chemistry, AlbaNova University Center, Royal Institute of Technology, S-106 91 Stockholm, Sweden*

Abstract

We have investigated the role of H-bonding on the static first-order hyperpolarizabilities of DNA base pairs, namely, adenine–thymine (AT) and guanine–cytosine (GC). To interpret the effect of long-range dipolar interaction on this optical coefficient, the configuration interaction method has been implemented in these systems. Remarkably, the static first-order hyperpolarizability values gradually increases for the AT base pair as one increases the H-bonding distance between the DNA bases, whereas a reverse trend is observed for the GC base pair where the hyperpolarizability values pass through a minimum.
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Deoxyribonucleic acid (DNA) plays a very significant role in biological systems as carrier of the genetic code. However, recent years have also witnessed this 'molecule of life' as a promising potential candidate in the rapidly emerging field of molecular nano-electronics [1–3]. The unique structure, some of the unique properties and its ability to self-assemble has resulted in new application areas for DNA like nanoscale robotics [4], DNA-based computation [5], as well as interesting applications in the field of photonics [1]. It has also been predicted that a truly conducting form of DNA will have a large impact on developments in the field of nanotechnology [3].

Several works have been carried out regarding the use of DNA in the field of electro-optics and photonics. In a very recent commentary, Steckl [1] highlighted this 'molecule of life' as an exciting new material for the fabrication of photonic devices with enhanced properties. In another recent study, Guerra et al. [2] have shown that substituted guanine–cytosine (GC) base pairs are more suitable candidates than the adenine–thymine (AT) base pair in the quest for chemically controlled nanoswitches. Apart from studies on optical properties of DNA, various investigations [6–8] have also been carried out on the stability of its double-helix structure. The H-bonds present in this double-helix structure play a crucial role in determining the stability of the DNA base pairs and hence the helical structure of DNA.

Albeit there have been a lot of studies on the optical properties of DNA and stability of the DNA base pairs, the issue about the variation of these properties with H-bonding distance still remains unresolved. In the present work, we offer an explanation on how the average static first-order hyperpolarizability values vary with the change in H-bonding distance between DNA bases in each of the base pairs using the configuration interaction (CI) method.

2. Computational details

Geometries for the DNA base pairs, i.e., adenine–thymine (AT) and guanine–cytosine (GC) have been optimized at the singlet state using B3LYP [9,10] type

---

* Corresponding author. Tel.: +91 33 23518386; fax: +91 33 23519755.
 E-mail address: swapanchem@yahoo.co.in (S. Chakrabarti).
[1] Fax: +46 8 5537 8590.

exchange-correlation functional and Pople's 6-31+G(d) basis set. For charge-transfer systems like AT and GC, the two-state model is quite effective in explaining the response properties. In this two-state formalism, the static first-order hyperpolarizability values depend on several factors, viz., the oscillator strength, f, the frequency of optical transition between the ground and first dipole allowed state, i.e., first excited state with highest oscillator strength, ω_{01} and the difference in moments between the ground-state and the first dipole allowed state, $\Delta\mu_{01}$. These factors have been determined at CI-singles (CIS) level of theory using 6-31+G(d) basis set in order to calculate the average static first-order hyperpolarizability values. It is to be noted that although we have carried out the CIS calculation on AT and GC base pairs for first three excited states, only the state corresponding to highest oscillator strength, i.e., first dipole allowed state is considered in this work and it is designated as state 1. All the calculations are carried out within the spin-restricted formalism using Gaussian 03 [11] suite of programs.

3. Results and discussion

The optimized geometries for the singlet state AT and GC base pairs are presented in Fig. 1(a) and (b), respectively, along with the H-bonds and ground-state energies. The energy values suggest the GC base pair (−937.5677 a.u.) to be more stable than AT (−921.5181 a.u.). There has been a significant disagreement between the theory and experiment regarding the H-bond lengths in DNA base pairs. In their work, Guerra et al. [6] for the first time had investigated the probable sources of this anomaly by studying several models for the AT and GC base pairs (present in the double-helix structure of DNA) at various levels of theory. They are of the view that source of this discrepancy might be the molecular environment of these base pairs in the crystals that are studied experimentally.

As mentioned above, DNA also found large applications in the field of electro-optics and photonics. In their work, Bertolotto et al. [12] reported the existence of a model which adequately describes the steady-state electro-optical behavior of DNA. In another work, Park and Stroud [13] described a model for structural development of a DNA/gold nanoparticle aggregate and calculated its optical properties. They also reported that using the optical and electrical sensitivity of this aggregate, biological detection is possible. Hence the role of DNA in these fields is of great significance and a study on the variation of the hyperpolarizability tensors (which is necessary for studying the optical properties) with the change in the H-bonds between the DNA bases makes sense.

In order to interpret the role of this H-bonding in explaining the response properties, namely, static first-order hyperpolarizabilities of these DNA base pairs, we perform an analysis by scanning the average values of this hyperpolarizability tensor over certain distances near the equilibrium separation, r_{eqm}. This scanning procedure is
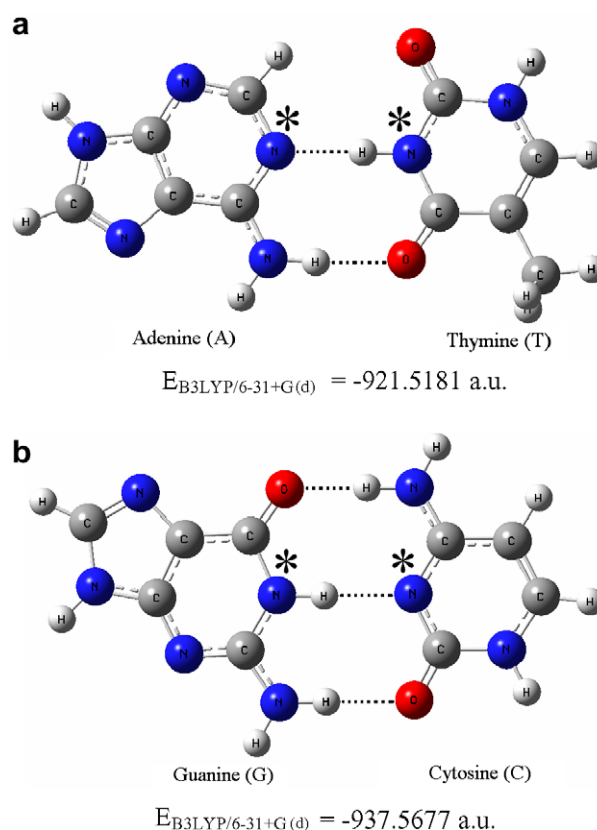

Fig. 1. Singlet state optimized geometries of (a) adenine (A)–thymine (T) and (b) guanine (G)–cytosine (C) DNA base pairs; the footnote of each structure contains the ground-state energies in a.u.

carried out by increasing as well as decreasing the distance between two nitrogen atoms (marked as * in Fig. 1(a) and (b)) from their equilibrium separation in each of the base pairs and determining the corresponding change in the above-mentioned property at each distance of separation.

Response properties in the static limit of a molecular system in general involves energy derivatives namely, polarizabilities and hyperpolarizabilities. The electric dipole moment can be expanded into different orders of external fields. It is represented as

$$\mu_a = \mu_a(E^b = E^c = E^d \cdots = 0) + \sum_b \alpha_{ab}E^b + \frac{1}{2}\sum_{bc}\beta_{abc}E^bE^c + \ldots$$

(1)

where $E^a(r,t)$, $E^b(r,t), \ldots$, are the external electric fields consisting of a monochromatic and a static part and the Cartesian directions $a, b, \ldots$ equal to $x, y,$ or z. In the expansion, the first term corresponds to permanent dipole moment of the sample. α_{ab} and β_{abc} represent the elements of linear polarizability tensor and first-order hyperpolarizability tensor, respectively.

There are several ways to evaluate the nonlinear optical coefficients of dipolar molecules. In an earlier work, Oudar and Chemla [14] proposed a two-state model relating nonlinear optical coefficient to the excited state energy, oscillator strength and dipole moment for some charge-transfer