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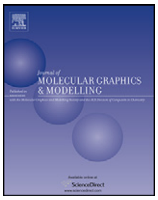

Effect of conformational degrees of freedom on the charge transfer in model tripeptide

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ABSTRACT

An extensive conformational dependence of the intramolecular charge transfer (both hole and electron) between intermediate residues of the model tripeptide in gas phase has been studied. The charge transfer integral, spatial overlap integral and site-energy for both hole and electron transfer between the intermediate residues in the tripeptides were calculated using the fragment orbital method. The site-energies and the charge transfer integrals have been calculated for different conformation of the glycine tripeptide by varying the dihedral angles (ϕ and ψ) along the α-carbon atom of amino acid subgroups. Electronic structure calculations show that the charge transfer integral between intermediate residues is strongly depending on the nature of the conformation of the peptide. The calculations indicate that the charge transfer is maximum at the particular conformation of the intermediate amino acid residues.

1. Introduction

The study of charge transfer in polypeptides has received a great deal of attention due to its relevance in biological activities and possible applications in molecular electronics [1]. The charge transfer (CT) in biological systems has been the subject of interest for experimental and theoretical investigations [2–7], especially in the long-range charge transfer through peptide bridging molecules and the kinetic study of intramolecular CT reactions based on the potential energy surface (PES) [8–24]. Isied and co-workers initially studied the long-range distance dependence of electron transfer process in peptides [25,26]. Serrano-Andrés et al. [27] have studied the charge transfer process in neutral and ionic polypeptides using ab initio and semi-empirical methods. They found that the charge transfer in their model di-, tri-, tetra-, and octamer peptides strongly depend on the type of conformation. Schanze and Sauer [28] have investigated the distance dependence of electron transfer with proline chains of varying length.

The peptide chain conformation through potential energy surface (PES) is a topic of biological importance. The biological activities of a peptide depend on its three dimensional structure and locations of basic sites in PES. The potential energy surface is defined as a function of Ramachandran and Sasisekharan [29] backbone dihedral angles along the α-carbon atom of amino acid subgroup, namely ϕ and ψ. The molecular conformations of an intermediate residues will affect the overall three dimensional shape of a protein, altering its structure and function in a biological system. Recently, Schlag et al. [30] have observed that the charge introduced in the polypeptide chain can stay within the subgroup, until the rotational angle reaches to a certain angle at which the charge is transferred to the next subgroup. In our previous studies, we found that, the calculated electron transfer rate for linear structure (for which $\phi = \psi = 180^\circ$) is relatively low, and both the hole and electron transfer rate is strongly depend on structural fluctuations of the intermediate amino acid subgroups [31,32]. Finklea et al. [33] concluded that the electron transfer rate through electroactive alkanethiol molecules can be increased through conformational changes of the chain. In our previous studies the charge transfer calculations were performed only for few particular standard conformations such as linear, α-helix, β-sheet and 3_{10}-helix [31,32]. Since, the proteins are in dynamical fluctuations with respect to the backbone dihedral angles, it would be of interest to investigate the conformational dependence of the charge transfer in model tripeptide through PES. The plot for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the amino acid subgroup (see Fig. 1) shows that the HOMO is delocalized on the region between α-carbon and nitrogen atoms of the amino group (i.e. N-terminus) and the LUMO is delocalized around the carbon and oxygen atoms of carbonyl group and not in the peptide linkage. DFT single point energy calculation also shows that HOMO of the fragments consisting of more than 75% of the nitrogen atom of the amino

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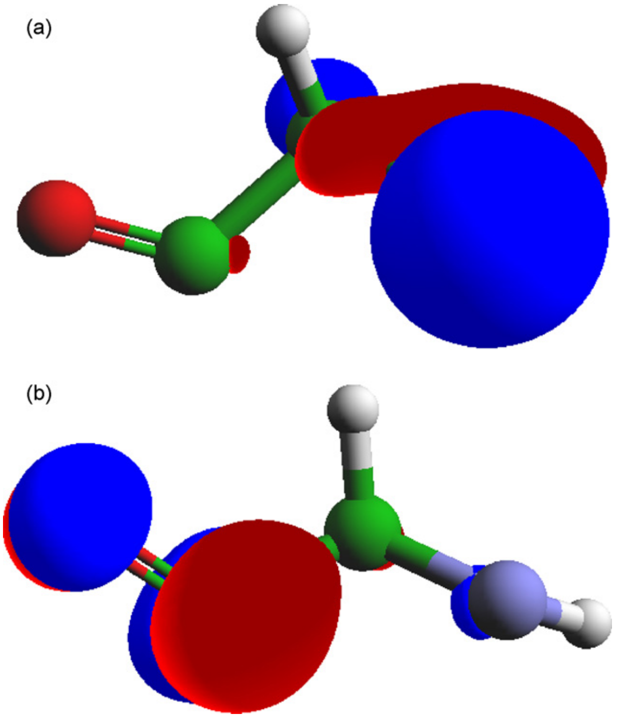


Fig. 1. The plot of (a) highest occupied molecular orbital and (b) lowest unoccupied molecular orbital of the of the amino acid subgroup ($NHCH_2CO$).

group and the LUMO consists of more than 65% of carbon and 25% of oxygen atoms of the carbonyl group. The HOMO and LUMO exhibit similar features of π-orbital and they are contributed from different atom pairs of amino acid subgroup. From this, we can expect, in polypeptide, if the α-carbon and nitrogen atoms of neighbouring amino acid subgroups are nearer then the hole transport is most favorable and if carbonyl group of each amino acid residues are nearer then the electron transport is most favorable.

The charge transfer integral (also called as electronic coupling or hopping matrix element) and site-energy (energy of the charge when it is localized at particular amino acid subgroup) corresponding to hole and electron transport are the key quantities that need to be calculated. In order to calculate the charge transfer integral and site-energy, a reasonable approximation has been made, the positive charge will migrate through the HOMO and the negative charge through LUMO of amino acid subgroups. We have calculated the charge transfer integral and site-energy for both hole and electron transport for a model tripeptide system based on fragment orbital approach method [31,32,34,35]. From this method the charge transfer integral and site-energy can be calculated directly as the off-diagonal and diagonal matrix elements of the Kohn-Sham Hamiltonian. This method is quite suitable to the present study since the site-energy of each amino acid subgroup in a tripeptide is not identical and the overlap between them is not equal to zero. In the next section, we present the theoretical methodology undertaken for the calculation of charge transfer integral and site-energy for hole and electron transport. Following this, we present the results and discussions. Finally, we conclude the paper with a summary of all our results.

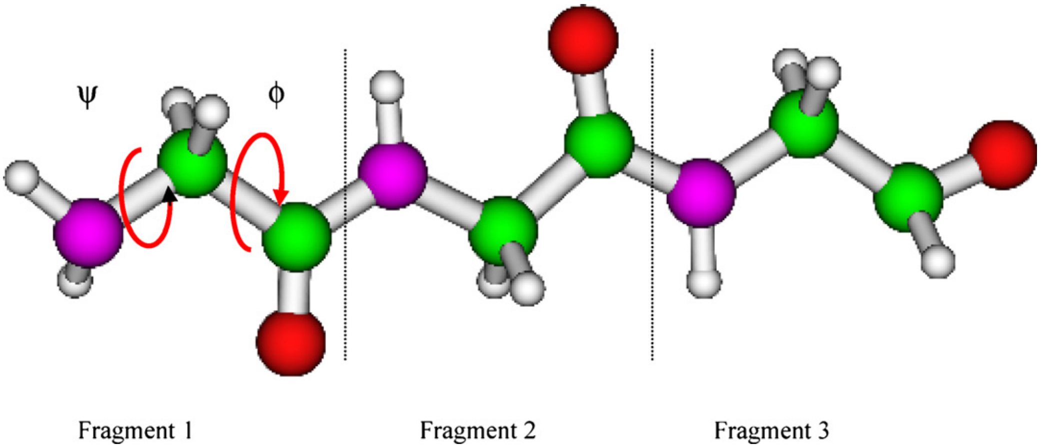
2. Methodology

The peptide conformations are characterized in terms of the dihedral angles along the α-carbon atom of the amino acid subgroups denoted as ϕ (*Phi*) and ψ (*Psi*) [36]. The model tripeptide which consisting of three glycine amide subgroups has been represented in terms of three fragments, as shown in Scheme 1. It is to be noted that here the fragments 1 and 3 are radical and fragment 2 is a bi-radical. In the present work the conformational properties of the tripeptide are investigated by the potential energy surface, which have been generated by varying the backbone dihedral angles (ϕ and ψ) in the increment of 30°. The geometries of 144 conformers of tripeptide have been optimized at B3LYP/6–311G(d, p) level of theory using Gaussian 98W program [37]. All the geometrical parameters (bond lengths, angles, and dihedrals) were fully relaxed, with the exception of the dihedral angles ϕ and ψ in all the subgroups.

The charge transport through peptide bond of model tripeptide is described by the tight-binding Hamiltonian method [38,39]. The Hamiltonian is given by

$$H = \sum_{i=1}^{n} \varepsilon_i(\theta(t)) a_i^{+} a_i + \sum_{i,j_{i \neq j}}^{n} J_{ij}(\theta(t)) a_i^{+} a_j \qquad (1)$$

In the above equation a_i^{+} and a_i are the creation and annihilation operators of a charge at the i^{th} amino acid subgroup in the tripeptide, $\varepsilon_i = \langle \varphi_i | H | \varphi_i \rangle$ is the site-energy of the charge and $J_{i,j} = \langle \varphi_i | H | \varphi_j \rangle$ is the charge transfer integral between HOMOs (or LUMOs) of subgroups i and j. In Eq. (1) both ε_i and J_{ij} depend on inter- and intramolecular degrees of freedom, collectively denoted as $\theta(t)$.



Scheme 1. The fragment representation of the model glycine tripeptide used for the charge transfer calculation.