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Ab initio quantum chemical study of electron transfer in carboranes

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Abstract

The electron transfer (ET) properties of 10- and 12-vertex carboranes are investigated by the ab initio Hartree–Fock method within the Marcus-Hush (MH) *two-state* model and the Koopman theorem (KT) approach. The calculated value of the ET coupling matrix element, V_{AB}, is consistently higher in the KT approach than in the MH *two-state* model. For the carborane molecules functionalized by –CH_2 groups at C-vertices, V_{AB} strongly depends on the relative orientation of the planes containing the terminal –CH_2 groups. The predicted conformation dependence of V_{AB} offers a molecular mechanism to control ET between two active centers in molecular systems.

1. Introduction

Carboranes are an important class of boron-containing rigid structures that have potential applications in medicinal drug design as hydrophobic pharmacophores [1], as antisense agents for antisense oligonucleotide therapy (AOT) [2], as boron carriers for boron neutron capture therapy (BNCT) [3–5], and as molecular probes for molecular medical diagnostics [6], among others. Recently, heteroisomeric diodes, based upon the chemical vapor deposition of different isomers of *closo*-dicarbadodecaborane, namely *closo*-1,2-dicarbadodecaborane (orthocarborane, C_2B_{10} H_{12}) and *closo*-1,7-dicarbadodecaborane (metacarborane, $C_2B_{10}H_{12}$), which have important applications as solid state neutron detectors have also been fabricated [7]. Due to their axially directed terminal bonds and rigid cage structures, carboranes also offer a unique opportunity in the area of molecular engineering for their potential application as a molecular anchor between two active reaction centers, and have been the subject of numerous experimental and theoretical studies [8–11]. It has been found that electron transfer (ET) across the carborane cage plays an important role in controlling the redox process in Ni-carboranes [12]. Therefore, an understanding of the electron transfer process across the carborane cages and its relationships to molecular geometry and electronic structure is deemed important. Such an understanding is also crucial for the future application of carboranes in molecular-scale electronics. It has recently been predicted [13–16] that σ-bonded carbon cage structures can be used as an effective electron tunnel barrier in molecular-scale electronic circuits.

In this Letter, we present ab initio investigations of the electronic structure and ET coupling strengths in *closo*-1,10-dicarbadecaborane ($C_2B_8H_{10}$), and *closo*-1,12-dicarbadodecaborane ($C_2B_{10}H_{12}$) and their –CH_2 derivatives, namely, 1,10-dimethylene-1,10-dicarba-*closo*-

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decaborane (H_2C-CB_8H_8C-CH_2), and 1,12-dimethylene-1,12-dicarba-*closo*-dodecaborane (H_2C-$CB_{10}H_{10}C$-CH_2). These carborane molecules will be referred to in the rest of this Letter as 10-vertex and 12-vertex carborane molecules, respectively. The ET coupling strength is calculated using the MH *two-state* model [17–21] within ab initio Hartree–Fock theory. The effects of basis sets and geometrical parameters on the ET coupling strength are also investigated. For comparison, the ET coupling strength is also estimated using the KT approach [17].

In Section 2, the computational approach employed in the present study is briefly described. The results and discussions follow in Section 3. The main findings of the present study are summarized in Section 4.

2. Computational approach

Ab initio Hartree–Fock (HF) and density functional theory (DFT) calculations of equilibrium geometry and electronic structure were performed with the GAUSSIAN quantum chemistry program package [22]. The geometrical parameters were obtained with the use of a minimal basis set (STO-3G) as well as an extended basis set consisting of a double zeta augmented by one *p* and one *d* polarization functions (DZP) as implemented in the Gaussian [22] basis set library. The extended basis set is referred to as the DZP basis set in the remainder of the Letter. In the DFT calculations, the B3LYP [23] exchange-correlation functional was employed.

The electron transfer coupling strength, V_{AB}, is calculated using the MH *two-state* (TS) model the details of which can be found in various review articles [17–21]. Briefly, the ET rate constant for a weak coupling (i.e., non-adiabatic limit) between electron donor and acceptor centers can be obtained from the Fermi Golden rule as [17]

$$K_{\mathrm{et}} = \frac{2\pi}{\hbar}|V_{\mathrm{AB}}|^2\mathrm{FCWD}, \quad (1)$$

where FCWD represents a Franck–Condon-weighted density of states, which reflects the nuclear modes of the system. The ET coupling matrix element, V_{AB}, which plays a major role in the ET process, represents the strength of the interaction between the two active reaction sites, and is given by [21]

$$V_{\mathrm{AB}} = (1 - S_{\mathrm{AB}}^2)^{-1}[H_{\mathrm{AB}} - S_{\mathrm{AB}}(H_{\mathrm{AA}} + H_{\mathrm{BB}})/2], \quad (2)$$

where

$$H_{\mathrm{AB}} = \langle \Psi_{\mathrm{A}}|H|\Psi_{\mathrm{B}}\rangle, \quad (3)$$

$$H_{\mathrm{AA}} = \langle \Psi_{\mathrm{A}}|H|\Psi_{\mathrm{A}}\rangle, \quad (4)$$

$$H_{\mathrm{BB}} = \langle \Psi_{\mathrm{B}}|H|\Psi_{\mathrm{B}}\rangle, \quad (5)$$

and

$$S_{\mathrm{AB}} = \langle \Psi_{\mathrm{A}}|\Psi_{\mathrm{B}}\rangle. \quad (6)$$

Here, S_{AB} is the overlap matrix element. H is the electronic Hamiltonian of the system, and Ψ_A and Ψ_B are the localized many-electron wave-functions of the two states A and B, respectively.

In the present study, the ab initio unrestricted Hartree–Fock (UHF) method was used to generate the localized states of the molecules. These localized wavefunctions were subsequently used as the initial guess in the self-consistent evaluation of the ET coupling matrix element. The nuclear configuration used for the calculation of the ET matrix element was taken to be the geometric average of the two localized structures, where $H_{AA} = H_{BB}$. It is important to note that Eq. (2) assumes the validity of the Condon approximation (i.e., V_{AB} is a weak function of the nuclear coordinates) in the vicinity of the transition state [17].

For the parent 10- and 12-vertex carboranes (i.e., $C_2B_8H_{10}$ and $C_2B_{10}H_{12}$), a symmetry-constrained optimization was performed to obtain the respective equilibrium structures. A model π-cage-π structure containing two active reaction centers was then constructed by replacing the terminal H atoms by –CH_2 groups yielding a *two-state* system. The resulting structures of the derivative carboranes are shown in Fig. 1 where the –CH_2 groups are the active reaction centers. The derivative molecules were then optimized in the singly positively charged doublet state. A pair of equilibrium structures, which by convention we term as left-localized and right-localized structures, were obtained by varying the C–C bond distance between the cage and each of the –CH_2 end groups, keeping the cage structure fixed.

The localized wavefunctions obtained for the derivative carboranes (i.e., $[C_4B_8H_{12}]^+$) and (i.e., $[C_4B_{10}H_{14}]^+$) were used as the initial guess for the calculation of the ET coupling element at the average of the left-localized and right-localized asymmetric configurations. In order to examine the effects of nuclear configurations on V_{AB}, *two-state* model calculations were also performed at one of the localized geometries, namely the left-localized asymmetric configuration. Calculations of V_{AB} in the *two-state* model were performed with the HONDO-8 electronic structure suite [24].

The V_{AB} of a singly-charged positive ion can also be calculated within the KT approach as [17]

$$V_{\mathrm{AB}} = 1/2(\varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{HOMO-1}}), \quad (7)$$

where ε_{HOMO} and ε_{HOMO-1} are energies of the highest occupied molecular orbital (HOMO) and the next highest occupied molecular orbital in the triplet state of the neutral molecule. The HOMO and HOMO-1 orbitals correspond to the symmetric and anti-symmetric combination of the p-orbitals of the terminal end groups, respectively. The KT approach has been successfully